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UPON THE SEPARATION OF THORIUM FROM THE RARE EARTHS OF THE CERIUM AND YTTRIUM GROUPS BY MEANS OF POTASSIUM HYDRONITRIDE.

BY L. M. DENNIS AND F. L. KORTRIGHT.

While engaged in other investigations on the rare earths, it was observed that when a solution of potassium hydronitride, KN_3, was added to the neutral nitrate solution of the earths extracted from the mineral sipylite, a white flocculent precipitate resulted, while by far the larger portion of the bases remained in solution. Both the original solution and the filtrate from the potassium-hydronitride precipitate showed strong erbium absorption-bands before the spectroscope. The precipitate was washed with water and dissolved in dilute nitric acid; this solution showed no absorption-bands.

From this it was evident that the potassium hydronitride had effected a fairly sharp separation of certain oxides from the mixture of earths present in the original solution. To ascertain the nature of the precipitate, the experiments were repeated with larger amounts of material, the earths from monazite being used, as our supply of sipylite was quite small.

Monazite sand from Brazil[1] was freed as far as possible from intermixed menaccanite by washing in a gold-washer's pan, and

[1] For the large amount (some 70 pounds) of this mineral placed at our disposal, we are indebted to the generosity of Professor Ricketts, of Columbia College, and Mr. G. O. Gordon, of New York City.

was then heated for several hours with concentrated sulphuric acid. The residue was introduced, in small amounts at a time, into ice-water, and was allowed to stand for several hours with occasional stirring. The clear supernatant liquid was then drawn off, and the ice-cold solution was precipitated at once with oxalic acid. The oxalates of the rare earths thus obtained were washed by decantation with hot water containing about one per cent. of hydrochloric acid, until the wash-water gave only a faint reaction for iron when shaken with potassium sulphocyanate and ether. The oxalates were then dissolved in concentrated nitric acid, most of the acid in excess was evaporated off, and the residue was dissolved in water, diluted, and precipitated by ammonium hydroxide. This precipitate was washed until free from lime and was then dissolved in hydrochloric acid. Hydrogen sulphide was passed through the hot solution for four hours. The flame was then removed, the current of hydrogen sulphide being continued over night. The very slight precipitate which formed was removed by filtration, the filtrate freed from hydrogen sulphide by heat, and the earths again precipitated by oxalic acid. This precipitate was washed with hot water containing a little hydrochloric acid to free it from the traces of iron which it still contained, and was then dried and ignited. The oxides thus purified were dissolved in nitric acid, most of the acid in excess was removed by evaporation, and the solution after dilution with water was nearly neutralized with dilute ammonium hydroxide. To this solution potassium hydronitride was added until a precipitate ceased to form. The white gelatinous precipitate settles quite readily if the solution of the earths be largely diluted before the hydronitride is added, or if a rapid current of air is driven through the solution after the addition of the reagent. The precipitate was washed by decantation with water until free from the mother-liquor and potassium salts. It was then dissolved in hydrochloric acid, and the solution precipitated by oxalic acid.

A portion of this precipitate, dissolved in nitric acid and evaporated to dryness, yielded a residue which gave no lines when tested in the Bunsen flame before the spectroscope. Moreover, the concentrated neutral nitrate solution of the precipitate showed no absorption-bands. A portion of this solution, diluted with an equal volume of water and boiled with lead dioxide, remained colorless, showing the absence of any appreciable amount of cerium.

From these experiments it seemed probable that the earth precipitated by potassium hydronitride was thoria. To test this supposition, the rare earths extracted from a sample of Norwegian thorite were dissolved in nitric acid, potassium hydroxide was added in excess, and chlorine was passed through the liquid and suspended precipitate for 24 hours. The precipitate still remaining was then filtered off, washed thoroughly, dissolved in hydrochloric acid, the solution precipitated by pure oxalic acid and the precipitate again carefully washed. To the nearly neutral nitrate solution prepared from this oxalate, potassium hydronitride was added in excess. A voluminous gelatinous white precipitate resulted. On adding ammonium hydroxide to the filtrate from this precipitate only a very slight precipitate appeared after some hours.

The equivalent of the earth precipitated by the potassium hydronitride from the monazite earths was then approximately determined by converting the earth into the oxalate, drying this at 100° C., weighing, igniting to constant weight and weighing the resulting oxide. Considering the composition of the oxalate dried at 100° C. to be $Th(C_2O_4)_2.2H_2O$, three determinations gave Th = 232.1, 232.7, 232.4 (O = 16), the results agreeing fairly well with the figures adopted by Ostwald as the most probable, namely, Th = 232.4.

Early in the work it was found that the potassium-hydronitride precipitate, on being heated on a platinum crucible-cover in the flame, simply dried down to a white powder without showing in the least the explosive quality possessed by other hydronitrides described by Curtius. A neutral solution of thorium nitrate was then prepared by adding to the slightly acid thorium solution ammonium hydroxide until a faint permanent precipitate formed. The precipitate was filtered off, and to the filtrate was added a neutral, odorless solution of potassium hydronitride. The usual precipitate resulted, and the characteristic odor of hydronitric acid became at once discernible, showing that when the thorium is precipitated by potassium hydronitride, some at least of the hydronitric acid is set free. A portion of the precipitate dissolved in nitric acid,[1] neutralized with potassium carbonate and acidified with acetic acid, gave no precipitate with silver nitrate. A test made in the same way with some potassium hydronitride gave a

[1] No odor of hydronitric acid was perceptible when this was done.

heavy precipitate. It thus appearing that the precipitate might be thorium hydroxide, an analysis was made of a freshly prepared portion. The precipitate was washed with water to remove the potassium salt, and was then filtered in an atmosphere free from carbon dioxide. The precipitate was dried in a tube at 100° in a current of air free from carbon dioxide. Weighed portions of the precipitate were then ignited and the residual thorium oxide weighed.

	Calculated for $Th(OH)_4$.	Found. I.	II.	III.
ThO_2	88.01	84.95	85.52	85.72

Although these results agree better with the hydroxide than with any other compound of thorium to be expected here, their great variation from the theoretical percentage made it seem probable that in spite of the precautions taken, the precipitate had absorbed carbon dioxide during the analysis. This supposition was borne out by the fact that on treating the dried precipitate with nitric acid, a gas was evolved which caused a turbidity in baryta-water. A repetition of the analysis was unfortunately impossible, as our supply of potassium hydronitride had been exhausted. A large amount of the reagent is now being made, with which further investigation of the nature of the precipitate and of the completeness of the separation from the other earths will be carried out.

Preparation of the Potassium Hydronitride.

The hydronitric acid was prepared by the method of Wilhelm Wislicenus,[1] the form of apparatus used being a slight modification of that proposed by Hopkins.[2] A sheet-iron cylinder, 12 cm. high and 8 cm. in diameter and closed at the bottom, is set into a large cylinder 15 cm. high and 13 cm. in diameter, the latter acting as an air-bath. The inner cylinder projects a short distance above the top of the large cylinder, and is provided with a tightly fitting iron cover. In this cover are three openings, one for the introduction of the ammonia or nitrous oxide, another for their escape, and the third for the thermometer. About 25 grams of metallic sodium is put in a small iron dish, and this is then placed in the inner cylinder. Dry ammonia gas is passed in, and the bath is heated by a Bunsen burner placed under the outer cylinder, to a temperature somewhat above 300° C. When the molten sodium

[1] Ber. d. chem. Ges. **25**, 2084. [2] Science **22**, No. 544, p. 1.

has been transformed to the amide, the temperature is lowered to from 200° to 230°, and nitrous oxide is run in. The sodium hydronitride is then dissolved in water, the solution acidified with dilute sulphuric acid, and the hydronitric acid is distilled over into water. The aqueous solution of the acid was then added to a solution of potassium carbonate until the reaction was quite strongly acid, and this was used in making the precipitation.

CORNELL UNIVERSITY, *December* 4, 1893.

ON THE COMPOSITION OF CERTAIN PETROLEUM OILS AND OF REFINING-RESIDUES.

BY CHARLES F. MABERY.

II.—THE SULPHUR COMPOUNDS IN OHIO PETROLEUM.

BY CHARLES F. MABERY AND ALBERT W. SMITH.

In a former paper[1] on the sulphur compounds in the Ohio petroleum we gave an account of results which seemed to indicate the presence in the products then examined of a series of sulphides homologous with methyl sulphide. These products were obtained from the Lima and Findlay wells, the principal localities in the United States for the production of the sulphur-petroleums. It was stated in that paper that the presence of substances other than sulphides had been observed, although they had not been obtained in quantities sufficient for examination.

It was with profound regret that an immediate continuation of this investigation was prevented by the pressure of other duties. In the meanwhile a paper was published by Kast and Lagai[2] of Karlsruhe which was devoted chiefly to a criticism of our results, without, however, offering any hint or suggestion toward the solution of the problem. The principal subjects of discussion in the paper last mentioned are the following:

1. Want of accuracy in our analytical data.

2. The formation of lead and calcium salts by neutralizing a solution of the sulphur-oils in sulphuric acid with lead or calcium carbonate, as the case required.

[1] This Journal **13**, 232. [2] Dingl. Journ. **284**, 69, Feb. 1892.

3. Failure by Kast and Lagai to obtain tangible (*fassbare*) products by treating the sulphur-petroleum distillates with mercuric chloride.

4. General inaccuracy of our work, and failure to interpret correctly the results we did obtain.

The several points of criticism will be considered in the order stated.

Our determinations of sulphur were made by the method of Carius, which we assumed was capable of affording accurate results in such sulphur compounds as we had under examination. But since the accuracy of this method is called in question by Kast and Lagai we have prepared ethyl sulphide by the very convenient method described in Levy's *Organische Präparate*, which consists in allowing ethyl chloride to act upon potassic sulphide in alcoholic solution. The crude product was submitted to fractional distillation, and 20 grams were collected that distilled at 91°–92° (barometer 747.6 mm.). Analyses of this product by the method of Carius gave the following results:

I. 0.1904 gram of the oil gave 0.4914 gram $BaSO_4$.

II. 0.2039 gram of the oil gave 0.5268 gram $BaSO_4$.

	Calculated for $(C_2H_5)_2S$.	Found. I.	Found. II.
Sulphur	35.55	35.46	35.48

Referring to notes of our former experiments, we find further evidence of the correctness of our analytical data. In an analysis by the Carius method of crude burning-oil distillate from Findlay petroleum, 0.3529 gram of the oil gave 0.0118 gram $BaSO_4$, which corresponds to 0.46 per cent. S. In a second analysis of the same oil by ignition with soda-lime, 3.8145 grams of the oil gave 0.1101 gram $BaSO_4$, which corresponds to 0.40 per cent. S. In the hands of inexperienced analysts, as Kast and Lagai observed, incomplete oxidation might interfere with accuracy in these determinations by Carius' method; but with an adherence to certain indispensable conditions of analysis we have had no difficulty in assuring ourselves of complete oxidation. To insure complete oxidation, fuming nitric acid to the extent of not less than twenty times the weight of the oil taken must be added, the sealed tube must be heated to 175° during fifteen hours, allowed to cool, opened to relieve the pressure, resealed, and heated to 240° during ten to twelve hours. Since fuming nitric acid attacks any

of these sulphur-oils with explosive violence, it is difficult to understand how loss by volatilization can be avoided in the method employed by Kast and Lagai, which depends upon oxidation in an open vessel by means of fuming nitric acid and potassic chlorate.

A considerable portion of Kast and Lagai's communication is devoted to a consideration of the formation of calcium or lead salts by neutralizing sulphuric-acid solutions of the petroleum-products with calcium or lead carbonate. The formation of salts was noted by one of us (C. F. M.) in earlier observations on the nature of these sulphur-oils and on the decomposition of the lead salt by evaporation. The decomposition-products of these salts were not then examined, although it was inferred from the dark color of the lead salt when its aqueous solution was evaporated that the salts were some form of sulphur compounds. Perhaps the inference of Kast and Lagai that we considered them to be sulpho-acid salts of the sulphides is justified by the form of statement which describes our observations on the character of these salts and the method we followed in the purification of the sulphur-oil. But, inasmuch as we had sulphides artificially prepared constantly at hand, and had repeatedly performed the experiment of dissolving ethyl sulphide in concentrated sulphuric acid and reprecipitating it by dilution, the exhaustive experiments of Kast and Lagai were not necessary to convince us that these sulphides form no sulpho-salts when dissolved in this manner. In fact, in recovering the sulphur-oils from the solution in sulphuric acid which had been used in refining, calcic hydrate was used simply as a convenient means of removing the acid completely, since otherwise much sulphurous acid was evolved during distillation, probably by reduction of the acid by the sulphides. In later study of sulphur-oils from other localities, calcic hydrate was not used, the oil being simply washed after precipitation by dilution. Our observation that the sulphur-petroleums contain certain constituents capable of forming salts receives confirmation at the hands of Kast and Lagai. But we had no intention of offering any suggestion as to the composition of these salts until we had given them further attention.

Referring to the third point of criticism in the paper of Kast and Lagai, in which they state that they were unable to obtain any definite (*fassbares*) product in fractions of lower boiling-points

from which we separated solid crystals, their results can be best stated in their own words: "Nun ensteht zwar auf Zugabe des Quecksilberchlorids eine deutliche Trübung, doch konnten wir ein fassbares Product auf dieser Weise nicht erhalten. Wir unterwarfen daher das rohe Oel der fractionirten Destillation, beobachteten aber schon bei 150° das Auftreten beträchtlicher Mengen von Schwefelwasserstoff. Um Zersetzung der Schwefelverbindungen hintanzuhalten, destillirten wir daher im luftverdünnten Raume bei einem Drucke von 45 mm. und wieder bis 150°. Das Destillat bildete ein klares, schwach gelblich gefärbtes Oel von intensivem Zwiebelgeruch. Den Rückstand bildete eine dunkelbraune, stark mit ausgeschiedenem Paraffin durchsetzte Masse."

The barrel of crude naphtha-distillate which we received from Findlay had been freshly distilled, and portions of it distilled in our hands without decomposition almost entirely below 150°, as described in our paper. When agitated with mercuric chloride a heavy precipitate separated in considerable quantities. The oil obtained from this mercury compound by decomposition with hydric sulphide could be distilled *in vacuo* nearly to the last drop without appreciable decomposition—certainly without the formation of "eine dunkelbraune, stark mit ausgeschiedenem Paraffin durchsetzte Masse," as Kast and Lagai assert.

As stated in our paper:[1] "All fractions containing sulphur gave precipitates with alcoholic and aqueous mercuric chloride, which were either crystalline or, with the less volatile products, thick viscous oils." We are frequently repeating these observations in the study of other oils.

Referring to our notes of experiments performed during March, 1890, in further confirmation of our former statements, we find that 800 grams of burning-oil distillate containing 0.43 per cent. of sulphur—from crude Findlay petroleum—were thoroughly agitated with aqueous mercuric chloride, the white solid pressed dry, pulverized, washed with light gasoline, again pressed and dried in the air. 70 grams of the mercury compound were thus obtained in the form of a fine white powder. 35 grams of this compound were triturated with an alcoholic solution of sodic sulphide, thoroughly shaken and allowed to stand over night. Upon diluting the filtered solution with water, 15 grams of the sulphur-oil sepa-

[1] *Loc. cit.*, p. 236.

rated, which by analysis was shown to contain 19.72 per cent. of sulphur. The remainder of the mercury compound was mixed with 250 cc. of alcohol, and hydric sulphide passed into the solution until it was saturated. The alcoholic solution upon dilution with water gave 11 grams of the sulphur-oil. This oil was nearly colorless, and when distilled under atmospheric pressure it began to collect at 140°; one-half distilled below 200°, and one-fourth between 200° and 250°; it changed color only very slightly during distillation.

In another experiment four liters of crude burning-oil distillate from Lima petroleum gave a crystalline mercury compound which, by decomposition with sodic sulphide, gave 15 cc. of the sulphur-oil containing 17.68 per cent. of sulphur. In one distillation of this oil under atmospheric pressure, two-fifths distilled at 100°–150°, two-fifths at 150°–250°, and one-fifth above 250°. 1200 grams of crude naphtha-distillate from Findlay petroleum were submitted to similar treatment, with the use of aqueous mercuric chloride to separate the sulphur compounds. The sulphur-oils recovered from the mercury compounds distilled between 100° and 200° under atmospheric pressure. From these results and the statements of Kast and Lagai given above, it is evident that the products they describe were wholly unlike those which formed the basis of our work.

Under the fourth head may be included such alleged inaccuracies of observation and experiment as Kast and Lagai have seen fit to infer from their study of products which appear from their statements to be widely different from those we examined. In the oil they procured in Bremen for Ohio oil they found 1 per cent. of sulphur, which they compare with the lower percentage reported by us. The numerous samples of Ohio oil which we have examined have never contained more than 0.6 per cent. of sulphur. From a few localities oils have shown more sulphur, but most of the results reported by other analysts have given about 0.5 per cent. In the report on the Ohio oil-fields, by Professor Edward Orton—published in the Eighth Annual Report of the United States Geological Survey—Professor N. W. Lord gives 0.553 per cent. as the quantity of sulphur which he obtained in crude Trenton limestone-oil. On the average the Ohio sulphur-petroleum employed in the preparation of commercial products contains 0.55 per cent. Sulphur-petroleums from other fields near at hand—such as the Canadian oils—contain more sulphur.

Kast and Lagai state that sulphur-oils could be deodorized by treatment with sulphuric acid without removing more than one-fourth of one per cent. of the total sulphur compounds. We have treated a sulphur-oil distillate containing 0.51 per cent. of sulphur with successive portions of sulphuric acid, determining the percentage of sulphur after each treatment. After agitating once with the acid, and washing thoroughly with sodic carbonate and water, the product was found to contain 0.20 per cent. of sulphur, and after the second treatment, 0.13 per cent. While a certain portion of the pungent odor had disappeared, the oil certainly was not deodorized to the extent mentioned by Kast and Lagai.

That crude distillates, especially those from Ohio petroleum, may be completely deodorized by agitation with aqueous mercuric chloride we have long been aware; in fact we have found this to be a convenient method for purifying crude or refined lighter distillates from sulphur-oils for laboratory use. To ascertain the extent to which mercuric chloride is capable of removing the sulphur compounds, we determined sulphur in the four liters mentioned above, from which was obtained 15 cc. of sulphur-oil. The percentage of sulphur was found to be 0.21, or two-thirds of the sulphur compounds were removed by this treatment. In another experiment the sulphur-oil distillate with 0.51 per cent. of sulphur, mentioned above, which came from Canada petroleum, after agitation with mercuric chloride gave by analysis 0.33 per cent. sulphur. There are, however, good reasons for the belief that the products from the Canadian oils contain sulphur in other forms than the paraffin alkyl sulphides. As to the odor of the crude oils, we cannot coincide with the inference of Kast and Lagai that it is due solely to unsaturated hydrocarbons. We believe it is caused rather by a mixture of bad-smelling compounds, and this opinion is supported by the fact that we have been able to separate several different classes of substances with penetrating, persistent odors. The presence of unsaturated hydrocarbons was clearly set forth in our former paper. That paper was devoted mainly to a description of results which seemed to indicate that the sulphides are the principal constituents of the sulphur-oils we examined, since they are extracted by sulphuric acid or by mercuric chloride, and we believed that the boiling-points, with the analytical data, and the general properties of the products isolated, constituted sufficient proof. It did not then seem necessary for further identifica-

tion to study the derivatives of the sulphides, more especially since, as was then stated, we collected several fractions with boiling-points widely different from those of known sulphides, which were reserved for careful study. Neither does it now seem advisable to repeat the vast amount of labor necessary to separate sufficient quantities of the same sulphides in order to form their oxidation-products for complete examination. We have frequently observed that oxidation by means of nitric acid converted any of these products into compounds with the acid which were heavier than water and sparingly soluble, and which were decomposed by sodic carbonate, leaving oils with the odor and general characteristics of the sulphoxides. By reduction with zinc and an acid the original compounds were recovered. In repeating these observations with small quantities of the sulphides which we fortunately found remaining from the examination of three years ago, we have found no difficulty in obtaining crystalline sulphoxides, although in quantities insufficient for individual identification. We therefore see no reason for a change in our belief concerning the presence in Ohio petroleum of sulphides, unsaturated hydrocarbons, and certain other products not yet fully identified.[1]

III.—PRELIMINARY EXAMINATION OF THE CANADIAN SULPHUR-PETROLEUM.

By Charles F. Mabery.

In continuing the study of the sulphur-petroleums, two years ago, with the assistance of Mr. William G. King, instructor in this laboratory, I undertook an examination of the Canadian sulphur-oils with the intention of pushing the work to final results as soon as possible. But the urgency of other affairs caused an unavoidable delay, and it was soon perceived that on account of the complexity of these products it would be necessary to manipulate considerable quantities of material in order to isolate interesting constituents which were present in small amounts.[2]

I had no intention of presenting any results of this investigation until it was completed, and the sole reason for this preliminary

[1] For the products which have enabled me to carry on this work I am indebted to the courtesy of the Standard Oil Company and of the Peerless Refining Company, through its superintendent, Mr. J. E. Bicknell. With larger quantities of the sulphur-oils I shall endeavor to separate and study more fully such other constituents as are present in smaller amounts.—C. F. M.

[2] For an ample supply of products from the Canadian oil-fields I am indebted to the generosity of Messrs. Samuel Rogers & Co., of the Queen City Oil Works, Toronto.

notice is the statement of Kast and Lagai that they propose to undertake the study of the sulphur-petroleums. Allusion has been made in a preceding paper to the fact that in less than one year after the publication of a paper by A. W. Smith and me on the Sulphur Compounds in Ohio Petroleum, Kast and Lagai published a criticism of our results and stated that they proposed to continue the study of the Ohio oils, notwithstanding the plain statement on our part of unfinished work that would be continued, and would include other products than those of the Ohio fields.

In beginning this work I procured from the Petrolia refinery of the company mentioned above twenty liters of crude petroleum, and ten liters of the "sludge acid" obtained in refining the burning-oil distillate. The crude petroleum was of a thicker consistency than the average Ohio oils; a determination of its specific gravity at 20° gave 0.86. The odor of hydric sulphide indicated some decomposition of the sulphur constituents. With the hydric sulphide removed it contained 0.98 per cent. of sulphur, as was shown in a determination by the Carius method. In distilling 1800 grams of the crude oil in a partial vacuum (under a tension of 250 mm.), below 150°, 195 grams, or nearly 11 per cent. was collected; between 150° and 300°, 435 grams, or 24 per cent.; and the residue above 300°, 1170 grams, or 65 per cent. The percentage of sulphur in the gasoline-distillate below 150° was shown in two determinations by the Carius method, the results being I, 0.52; II, 0.47 per cent. A determination of sulphur in the burning-oil distillate by the same method gave 0.64 per cent. The residue above 300° contained 0.98 per cent. of sulphur.

A perceptible odor of sulphurous acid in the acid solution of the sulphur-oils indicated certain decomposition. The oil held in solution in the acid was precipitated by pouring into water—slowly, to avoid heating—and it was washed free from the acid with sodic carbonate and water. The quantity of oil thus obtained was nearly equal in volume to one-half of the original acid solution. It was dark-brown in color and nearly opaque, with the consistency approximately of the crude Canada petroleum. A determination of its specific gravity at 15° gave 0.86. It contained 9.94 per cent. of sulphur, as shown in a determination by the Carius method. In distilling this oil with steam, the steam-distillate was not seriously decomposed, although hydric sulphide and sulphurous acid were evolved to some extent. After thorough washing

and drying with calcic chloride it gave upon analysis 5.46 per cent. of sulphur. The residue of the distillation with steam was thicker and heavier than the original oil; its specific gravity at 15° was found to be 0.97, and it contained 10.41 per cent. of sulphur. The predominating odor of the steam-distillate was even more strongly penetrating than the aromatic odor previously described as present in the Ohio oils. The steam-residue retained the same odor in a far less degree, its odor resembling more especially that of the sulphides. When redistilled under atmospheric pressure the steam-distillate collected without much decomposition below 200°. A determination of its specific gravity at 20° gave 0.82.

In attempting to subject these products to fractional distillation, a serious difficulty was encountered in the persistency with which the oils retained water, especially those of higher boiling-points. Even after standing several weeks in contact with fused calcic chloride, sufficient water remained in some instances to prevent distillation. The ordinary means for preventing explosive formation of vapor, or "bumping," such as introduction of glass beads or platinum, or passing into the flask a current of inert gas during distillation, failed utterly; in one instance a round hole was blown through the bottom of the flask, letting out the oil into the lamp flame. Even when the oil seemed perfectly dry it was nearly impossible to distil it quietly; the only possible way to distil several of these fractions was to keep the distillation-flask constantly in motion. This difficulty was doubtless caused, at least partially, by the tendency of the oils to decomposition. In one fraction of the residue from the distillation with steam, which began to distil under a tension of 100 mm. above 220°, the decomposition was very marked:

Temperature.	Pressure.
240°	55 cm.
250°	50
287°	47
292°	40
300°	30
Temp. fell to 271°	17

Considerable sulphur separated during this decomposition.

That portion of the residue from the distillation with steam, with lower boiling-points, was submitted to ten fractional distillations, collecting the distillates at intervals of 10° up to 250°, under a tension of 150 mm. Determinations of sulphur in two fractions gave the following results:

	69°–72°.	96°–97°.
Percentage sulphur	9.12	12.96

These fractions all gave crystalline or viscous precipitates with mercuric chloride, leaving an oil lighter than water, with an intensely penetrating odor, indicating the presence of an homologous series of compounds quite different in their character from the principal constituents. The oils with the peculiar odors elsewhere mentioned as constituents of the Ohio petroleums are apparently present in these oils in larger quantities.

The steam-distillate was redistilled six times under a tension of 150 mm., and collected at intervals of 10° from 32° to 200°. Each fraction united with great energy with bromine, leaving no residual oil, thereby showing the absence of hydrocarbons homologous with methane. Determinations of sulphur in several fractions gave the following results:

Fraction	32°–40°	40°–70°	110°–120°
Sulphur	0.43	0.65	11.51
Fraction	120°–130°	140°–150°	160°–170°
Sulphur	13.04	13.44	13.93

The lower fractions unite readily with bromine, leaving no residual paraffin hydrocarbons, and with hydrobromic acid, thus proving their identity as unsaturated hydrocarbons. They polymerize with great readiness after long standing; one fraction, 32°–40°, when redistilled under atmospheric pressure, after standing two years, when a little had passed over, suddenly decomposed into a thick viscous oil with a rise in temperature above 150°.

In resuming this investigation recently, with the aid of Mr. W. O. Quayle, instructor in this laboratory, appreciating the necessity of working with larger quantities of these oils, I have procured from Petrolia 225 liters of the oil precipitated from the acid solution obtained in refining burning-oil distillates. When received, this oil contained no hydric sulphide and was strictly neutral in its

reaction; it contained no sulphuric acid. Unlike the product formerly examined, this oil suffers serious decomposition when distilled with steam, with the evolution of hydric sulphide, sulphurous acid, sulphuric acid and sulphur. Even when distilled *in vacuo*, if the air is not nearly all withdrawn, there is much decomposition, which is undoubtedly caused by the presence of exceedingly unstable sulphur compounds. Before distillation the oil as it was received was dried as thoroughly as possible by standing a week or longer with large quantities of freshly fused calcic chloride. Even after long standing, however, a small amount of water has remained unabsorbed, perhaps to the extent of 10 cc. in 15 liters. In a porcelain still of 15 liters capacity we have distilled 150 liters under a tension of 45 mm., collecting below 150°, 150°–250°, and above 250°. The decomposition was comparatively slight, although it was impossible to avoid some evolution of hydric sulphide and sulphurous acid, with some sulphur from the action of these gases upon each other. After thorough washing and drying, these distillates will be subjected to prolonged fractional distillation in porcelain stills.

The peculiar odors of all these products are strongly marked, especially a garlic odor attacking the eyes, which is readily distinguishable by persons unaccustomed to laboratory smells, as well as the peppermint odor previously mentioned; and after precipitation of the sulphides with mercuric chloride an oil has been separated with an odor closely resembling that of oil of turpentine. It is expected that the substances which occasion these odors will be separated in the distillation of the large quantities of material which we now have under examination.

CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE, *November* 1, 1893.

SOLUBILITY OF METALLIC OXIDES IN NORMAL POTASSIUM SALTS OF TARTARIC AND OTHER ORGANIC ACIDS.

By Louis Kahlenberg and H. W. Hillyer.

Part I.—Experimental.

Lead Monoxide and Normal Potassium Tartrate.

It was observed that lead monoxide, when added to a boiling solution of normal potassium tartrate, is dissolved with readiness, imparting to the liquid a strongly alkaline reaction and a soapy feel, not unlike that of a strong solution of caustic alkali. The primary purpose of the work undertaken is to investigate this reaction.

Normal potassium tartrate was first treated with lead oxide, in order to determine how much of the latter would be dissolved by a certain amount of tartrate. The normal potassium tartrate was prepared by exactly neutralizing a definite amount of tartaric acid with a normal solution of potassium hydroxide. Thus a known amount of the normal tartrate was at once obtained in solution. This solution was then treated with lead oxide.

The tartaric acid used was a well crystallized sample of Trommsdorff's make. 1.0124 grams of the acid were dissolved and titrated with a normal solution of potassium hydroxide, using phenolphthaleïn as indicator. It required 13.55 cc. of the alkali to neutralize this amount of acid. Theory requires 13.5 cc., showing that the acid was very pure. The lead oxide was of Merck's make, and was also tested as to its purity: 5.6833 grams were treated with nitric acid; a very slight residue of lead peroxide remained undissolved, indicating the presence of traces of minium. The amount, however, was not sufficient appreciably to affect the accuracy of the experiments. The solution in nitric acid was evaporated to drive off the excess of acid. The lead was precipitated with sulphuric acid, alcohol was added, and after standing for about six hours the lead sulphate was filtered off, and the filtrate evaporated to dryness. No residue remained, showing that the lead oxide was free from alkali.

6.7059 grams of tartaric acid were exactly neutralized with potassium hydroxide, and the solution, amounting to about 300 cc., was treated in a casserole with a slight excess of lead oxide, the quantity used being accurately weighed. The mixture was boiled for half an hour, the water evaporated being replaced from time to time. The liquid was then filtered through a hot-water funnel, the residue of lead oxide thoroughly washed with boiling water, dried and weighed. The weight of the residue subtracted from the total amount of lead oxide taken gave the amount dissolved by the tartrate. In this way it was found that 10.1144 grams of normal potassium tartrate (corresponding to 6.7059 grams of acid) took up 11.175 grams of lead oxide. If one molecule of tartrate reacted with one molecule of oxide, and no more, 10.1144 grams of tartrate would dissolve only 9.9801 grams of oxide. However, we found in this experiment that 10.1144 grams of tartrate dissolved 11.175 grams of oxide; that is, one molecule of tartrate dissolved 1.1197 molecules of lead oxide.

A second experiment similar to the one just described, except that the solution was kept slightly more concentrated, yielded a somewhat different result: 4.7725 grams of normal potassium tartrate in 100 cc. water were treated for half an hour at a boiling heat with lead oxide; it was found that 5.3637 grams of lead oxide were dissolved; that is, one molecule of tartrate took up 1.1389 molecules of lead oxide under these conditions.

A third experiment was conducted as follows: 1.8532 grams of potassium tartrate in 50 cc. water were treated for six hours with about 4.5 grams lead oxide in a small casserole on a calcium-chloride bath containing 50 per cent. of calcium chloride. The liquid was kept boiling, was stirred occasionally, and the water evaporated was replaced from time to time. At the end of six hours the liquid was filtered, the residue of lead oxide thoroughly washed with hot water, and the filtrate diluted to 250 cc. 100 cc. of this solution were taken and the lead determined as sulphate. From the 100 cc., 1.2266 grams of lead sulphate were obtained, corresponding to 0.9027 gram lead oxide. Under these conditions, then, 1.8532 grams normal potassium tartrate took up 2.2568 grams lead oxide, or one molecule of tartrate reacted with 1.2341 molecules of lead oxide.

It appears, then, that the amount of lead oxide dissolved by normal potassium tartrate depends upon the concentration of the

solution, and upon the length of time of boiling. It was observed, however, that one molecule of oxide is taken up by one molecule of tartrate with comparative readiness, while after the introduction of one molecule of lead oxide more could be dissolved only with great difficulty. It was observed that 10.1144 grams of potassium tartrate in 300 cc. water dissolved a quantity of lead oxide corresponding to one molecule for every molecule of tartrate, on boiling for ten minutes, while boiling for half an hour caused only 1.1197 molecules of lead oxide to go into solution.

When the hot solution of lead oxide in normal potassium tartrate is dilute—as for instance in the case just mentioned—it remains clear on cooling; if it is somewhat more concentrated, there separates out on cooling a white precipitate, in appearance not unlike aluminium hydroxide. When alcohol is added to the clear solution, a similar precipitate forms.

It was attempted to isolate the compound formed by the action of lead oxide on normal potassium tartrate. All attempts to obtain crystals from the clear aqueous solution proved futile. The substance invariably separated out as a white slimy precipitate, even when slowly evaporated over sulphuric acid under the bell-jar.

The method of precipitating with alcohol was next tried. Alcohol was added to the clear aqueous solution of lead oxide in normal potassium tartrate so as to precipitate out a part of the lead salt. The precipitate was filtered off, and to the filtrate more alcohol was added, to cause a second precipitate, which was also filtered off. Again alcohol was added to the second filtrate, causing a third precipitate, which was filtered off. All three precipitates were washed several times with dilute alcohol, dried at 110° C. in an atmosphere freed from carbon dioxide, and analyzed. The combustions were carried out with a mixture of lead chromate and potassium bichromate.

The results of the analyses of the three precipitates are here tabulated:

	No. 1.		No. 2.	No. 3.
Pb	56.45	...	56.40	56.73
K	10.22	...	10.96	10.58
C	9.30	9.09	...	...
H	0.89	0.93	...	...

Although the results of the analyses agree fairly well—the only instance in which there is a difference exceeding the limit of error

being in case of the percentages of potassium found—they do not lead to a formula for a tartrate; so that we were dealing either with a mixture or we had changed our tartaric acid. That the former was the case, and not the latter, soon became apparent. The experiments that established this fact will be described below.

It was thought desirable to analyze the precipitate that separates on cooling a hot concentrated solution of lead oxide in potassium tartrate. Accordingly such a precipitate was prepared. It was thoroughly washed with water until nearly half of the precipitate was washed through the filter. Finally it was dried at 120° C. in an atmosphere free from carbon dioxide, and analyzed according to the method already described.

0.7453 gram substance yielded 0.8416 gram $PbSO_4$ = 0.575 gram Pb = 77.15 per cent. On combustion with lead chromate and potassium dichromate: 1.0195 grams substance yielded 0.0598 gram H_2O = 0.0066 gram H = 0.65 per cent.; and 0.2233 gram CO_2 = 0.0609 gram C = 5.97 per cent. Potassium was absent. These results lead to the empirical formula $(PbO)_2C_4H_4O_6Pb$; that is, the substance is a very basic lead tartrate. The results are here tabulated:

	Calculated for $(PbO)_3C_4H_4O_6Pb$.		Found.
C	5.99		5.97
H	0.50		0.65
Pb	77.15		77.52
O	16.36	(By difference)	15.86

It was thought that probably this same salt might be obtained by thoroughly washing with water one of the precipitates obtained by adding alcohol to the clear solution of lead oxide in normal potassium tartrate. Accordingly a solution of potassium tartrate was treated with lead oxide in excess for half an hour. The excess of oxide was filtered off and alcohol added to the clear filtrate. The precipitate thus formed was washed with water until fully one-half of it was washed through the filter. The remainder was then dried at 120° C. as before and analyzed. For convenience of comparison the results of this analysis and those of the preceding experiment are here given in tabular form:

	$(PbO)_2C_4H_4O_6Pb$. Found.	Precipitate by Alcohol. Found. I.	II.
C	5.97	7.3	7.17
H	0.65	0.67	0.75
Pb	77.52	70.39	...
K	...	3.79	...

It appears, then, that the precipitate by alcohol contains an appreciable amount of potassium which cannot be removed by washing with water, and that this precipitate is really a mixture of potassium tartrate and a basic lead tartrate.

To prove that tartaric acid remains unchanged when normal potassium tartrate is treated with lead oxide, the following experiment was undertaken: A solution of normal potassium tartrate was boiled with an excess of lead oxide as before, and the excess of oxide filtered off. To the clear filtrate a solution of lead acetate was added, and then acetic acid sufficient to acidify. The normal lead salt of the acid was thus precipitated. The precipitate was washed, suspended in water, decomposed with hydrogen sulphide, the lead sulphide filtered off, and the filtrate containing the free acid evaporated to crystallization. The crystals obtained had the characteristics of those of tartaric acid and left no residue on ignition, showing that they contained neither potassium nor lead. They melted at the same temperature as crystals of tartaric acid tested side by side with them. 0.498 gram of the crystals dissolved in water and titrated with normal potassium hydroxide, required 6.6 cc. of the alkali to neutralize. Theory requires 6.64 cc. A second sample of 0.57 gram required 7.6 cc. normal potassium hydroxide. Theory requires 7.6 cc. The fact that tartaric acid has remained intact is thus established.

From the strongly alkaline solution of lead oxide in normal potassium tartrate, the lead is precipitated as sulphide by hydrogen sulphide and as carbonate by carbon dioxide. In each case, after complete precipitation, the clear supernatant fluid has a neutral reaction. Nitric or acetic acid added to a clear solution of lead oxide in potassium tartrate causes the formation of a precipitate. It was determined to find out the extent of the alkalinity of the solution of lead oxide in potassium tartrate by titrating with a normal solution of nitric acid, using phenolphthaleïn as indicator. A normal solution of hydrochloric acid may also be used if the solution is sufficiently dilute and warmed so as to prevent lead chloride from separating out. Accordingly 4.0498 grams of tartaric acid were neutralized with 54.1 cc. of a normal solution of potassium hydroxide. The normal salt thus obtained was treated with an excess of lead oxide, the solution filtered, the residue thoroughly washed with hot water, and the clear filtrate diluted to 700 cc. 100 cc. of this solution required 4.3 cc. of the normal

nitric-acid solution to neutralize it, equivalent to 30.1 cc. acid for the 700 cc., or an amount of acid corresponding to 55.5 per cent. of the whole amount of the normal solution of potassium hydroxide required to prepare the original potassium tartrate. As the titration proceeds, the permanent precipitate forms a little before the neutral point is reached. Because of the presence of the heavy precipitate, it is somewhat difficult to tell just when the point of neutrality has been reached. The end of the reaction can best be judged when the precipitate is allowed to subside after each fresh addition of acid.

In a second similar experiment, in which 19.1 cc. of the normal solution of potassium hydroxide were used to prepare the normal tartrate, 10.5 cc. acid were used to neutralize the solution (solution of lead oxide in normal tartrate), or an amount equivalent to 54.97 per cent. of the normal alkali used. Both the point of neutrality of the solution of lead oxide in normal potassium tartrate, and that at which a permanent precipitate is formed during the process of titration, depend on the amount of lead oxide that has been dissolved by the given amount of normal tartrate. And, as the quantity of lead oxide taken up by a certain amount of tartrate varies slightly under different conditions, as we have seen, one can hardly expect to obtain closely agreeing results from two independent experiments, because of the difficulty of keeping two solutions of potassium tartrate exactly the same, as to concentration and length of time of treatment, during the process of saturating them with lead oxide.

That free potassium hydroxide is formed when lead oxide and normal potassium tartrate are boiled together was shown by the following experiment. Normal potassium tartrate was boiled with an excess of lead oxide for half an hour. The whole was then rapidly evaporated to dryness over the free flame and extracted with alcohol. The alcoholic liquor was poured off through a filter and evaporated to dryness. The residue was free from lead and had the characteristics of potassium hydroxide. An aqueous solution of it precipitated hydroxide of copper from a copper sulphate solution, ferric hydroxide from a solution of ferric chloride, and zinc hydroxide (soluble in excess) from a solution of zinc sulphate.

If we dissolve one equivalent of lead tartrate in two equivalents of potassium hydroxide, we get a solution which is identical with

that obtained by dissolving one equivalent of lead oxide in one equivalent of potassium tartrate, as is shown by the following experiment: To a solution of 0.626 gram of tartaric acid a slight excess of lead acetate was added. The precipitate of lead tartrate was filtered off, washed with water and dissolved in 8.35 cc. of the normal solution of potassium hydroxide, an amount just sufficient to neutralize the tartaric acid taken. The solution, amounting to 50 cc., was titrated with a normal solution of acid. It was found that 4.1 cc. of the acid were required to secure neutrality toward phenolphthalein.[1] It is necessary, then, to neutralize one-half of the potassium used in preparing the solution in order to secure neutrality. The same result is obtained when 0.626 gram of tartaric acid is first neutralized with 8.35 cc. of normal potassium-hydroxide solution, 9.306 grams lead oxide—the amount corresponding to one molecule of oxide for one molecule of tartrate—dissolved in the solution and the whole titrated with normal acid solution. This proves that the solution containing one molecule of lead tartrate *plus* two molecules of potassium hydroxide is the same as the one containing one molecule of potassium tartrate *plus* one molecule of lead oxide. Furthermore, the rotatory powers of the solutions are identical, as will be shown in a subsequent paper.

Since lead tartrate dissolves in a quantity of potassium-hydroxide solution equivalent to the tartaric acid taken to prepare the tartrate, giving the solution an alkalinity equal to one-half the alkali used, it was thought that lead tartrate would very likely dissolve in less potassium hydroxide than the amount required to neutralize the tartaric acid. This proved to be true. Lead tartrate prepared as before from 0.626 gram tartaric acid required 5.5 cc. of normal potassium-hydroxide solution for its complete solution. The precipitate was suspended in about 10 cc. of water and the alkali added drop by drop from a burette, the liquid being continually stirred. The solution had an alkaline reaction. That only a slight excess of alkali had been used was shown by the fact that on adding two drops of normal nitric-acid solution to one-fifth of the solution (which had been made up to 50 cc.) a permanent precipitate was formed. Neutrality toward phenolphthalein was not obtained, however, until 0.3 cc. normal acid

[1] A permanent precipitate forms a little before the last of the acid is added.

had been added, making 1.5 cc. acid necessary to neutralize the whole 50 cc. Since the whole amount of normal potassium-hydroxide solution required to neutralize the 0.626 gram tartaric acid is 8.35 cc., it is clear that the amount of potassium hydroxide that can be titrated with standard acid is that which is in excess of one-half the quantity of potassium hydroxide necessary to neutralize the tartaric acid taken. This result is in accord with the fact already mentioned that when one molecule of lead tartrate is dissolved in two molecules of potassium hydroxide, only one molecule of potassium hydroxide exists in the solution so that it can be titrated.

Lead Oxide with other Normal Tartrates.

The normal tartrates of sodium and potassium, sodium, lithium, and rubidium, like the normal tartrate of potassium, dissolve lead monoxide with considerable readiness. On the other hand, thallium tartrate and potassium antimonyl tartrate do not act on lead oxide. On treating ammonium tartrate with lead oxide, ammonia is liberated. The lead salt formed is soluble in hydroxide of ammonium. When potassium ethyl tartrate is treated with lead oxide, it is saponified. The resulting white lead salt goes into solution only upon addition of an alkaline hydroxide.

With normal sodium tartrate experiments were performed similar to those already described with potassium tartrate. The results agree closely with those found in case of that salt.

A study of the rotatory power of the solutions of lead oxide in normal alkali tartrates has yielded some interesting results which will appear in the subsequent article already mentioned.

Potassium Tartrate with Other Oxides.

It was also undertaken to find out what oxides besides that of lead would react with normal potassium tartrate. Accordingly the oxides having the following formulas were treated with potassium tartrate: As_2O_3, Sb_2O_3, SnO_2, Bi_2O_3, HgO, Ag_2O, Pb_3O_4, CuO, Fe_2O_3, Al_2O_3, Cr_2O_3, MnO_2, ZnO, MgO, BeO, Er_2O_3, Ce_2O_3, Di_2O_3, UO_2. The treatment consisted of adding some oxide to the solution of potassium tartrate in a casserole and boiling the mixture over the free flame for from fifteen to thirty minutes. In the case of arsenious oxide, a slight amount of the oxide passed

into solution, but this might have been expected, as this substance is somewhat soluble in water. A very small quantity of mercuric oxide was also dissolved by treating it with potassium tartrate; and from the solution on cooling or on standing for twenty-four hours, mercury separated in the form of a mirror on the surface of the liquid and on the sides of the vessel. The other oxides were not attacked by the tartrate solution. Cupric and chromic hydroxides were also treated with potassium tartrate, but were not dissolved. In respect to its action on normal potassium tartrate, then, lead oxide seems to stand quite alone.

It has long been known to analytical chemists that the presence of tartrates (and also of salts of other hydroxy acids) in a solution prevents the precipitation of many heavy metals by caustic alkalies. It appears, then, that though potassium tartrate prevents the precipitation of the heavy metals by potassium hydroxide, it is not able to dissolve their oxides when once they are formed. The most prominent example of this, perhaps, is Fehling's solution. Here potassium tartrate prevents the precipitation of copper by caustic alkali, and yet potassium tartrate will dissolve neither the oxide nor the hydroxide of copper.[1]

Lead Oxide and Salts of Other Acids.

The question arises, What other organic acids are there whose alkali salts dissolve lead monoxide? To investigate this question, the potassium salts of the following acids were prepared and treated with lead oxide: succinic, malonic, malic, citric, acetic, propionic, lactic, glyceric, saccharic and mucic. As before, the aqueous solution of the salt was boiled with lead oxide in a casserole over the free flame from fifteen to twenty minutes. Both moderately dilute and strongly concentrated solutions of the salts were thus treated.

Potassium malate, citrate, lactate, and glycerate, in strongly concentrated solutions, take up insignificant quantities of lead oxide on long-continued boiling. The salts of the other acids mentioned, excepting those of saccharic and mucic acids, do not act on lead oxide.

[1] It should be stated here, perhaps, that the precipitate obtained on treating a solution of copper sulphate with potassium hydroxide in the cold consists to a considerable extent of a basic copper salt which will dissolve in potassium tartrate. When copper sulphate solution is treated with potassium hydroxide at a boiling heat, the black precipitate obtained, consisting partly of cupric oxide and partly of cupric hydroxide, does not dissolve in potassium tartrate.

Lead oxide forms with potassium saccharate, and also with potassium mucate, a difficultly soluble tribasic lead salt, the saccharate being slightly more soluble than the mucate. It was found that one molecule of saccharate reacts with two molecules of lead oxide; the same is true of potassium mucate. The experimental data are as follows: 1.5087 grams of normal potassium saccharate were prepared by neutralizing with 10.55 cc. of a normal solution of potassium hydroxide, 48.6 cc. of a solution of saccharic acid whose strength had previously been determined by titrating, at a boiling heat, with a normal solution of potassium hydroxide, using phenolphthalein as indicator. The potassium saccharate solution was boiled with a known excess of lead oxide over the free flame, the solution being constantly stirred, and the volume of the liquid kept as small as possible without running risk of spirting. At the end of half an hour the liquid was diluted with sufficient boiling water to dissolve the white salt formed, and was filtered through a hot-water funnel. The concentrated filtrate was set aside to cool, and on cooling a white precipitate formed. The residue on the filter, consisting of the excess of lead oxide together with some of the lead saccharate, was then very thoroughly washed with boiling water. It was found impossible, however, to free the lead oxide from small quantities of the lead saccharate, so that on weighing back the residue of lead oxide, the result was a little too high, making the amount of lead oxide that combined with the potassium saccharate as found by experiment rather low. By subtracting the weight of the residue of lead oxide from the total amount of lead oxide taken, it was found that 1.5087 grams of potassium saccharate react with 2.2750 grams of lead oxide. If one molecule of potassium saccharate reacts with two molecules of lead oxide, theory requires that 1.5087 grams of saccharate should take up 2.3527 grams of lead oxide.

As already stated, a white precipitate separated out of the concentrated filtrate from the excess of lead oxide. This was filtered off and washed several times with water. The precipitate has a great tendency to pass through the filter, and the opalescent appearance of the filtrate, which becomes more marked when a little alcohol is added to it, reminds one of finely divided titanic acid suspended in a solution. The precipitate was dried at 110° in an atmosphere free from carbon dioxide, and 1.022 grams of the white granular salt thus obtained were analyzed. The salt

contained no potassium, and yielded 1.1152 grams $PbSO_4$ = 0.7619 gram Pb = 74.55 per cent. The theory for $C_6H_4O_6Pb_2$ is 75.27 per cent. This shows that the salt dried at 110° probably contains some water; but as the salt readily decomposes at a higher heat, and as the quantity of substance at disposal was small, no further tests were made with it.

2.4882 grams of normal potassium mucate were prepared in a manner similar to that used in the preparation of the saccharate. The aqueous solution was then treated, as in the case of the saccharate, with a known excess of lead oxide for half an hour. However, the lead mucate formed was so difficultly soluble that it could not be separated from the residual lead oxide by filtration. Another process had to be adopted: the lead salt was separated from the residual lead oxide by taking advantage of the fact that the oxide is heavier than the salt and hence sinks to the bottom of the dish more readily. The lead salt was poured off with the supernatant liquid, and a small spoon was used to make the separation as complete as possible. This crude method, of course, could not yield sharp analytical results, but it was the best one that suggested itself. On weighing back the residual lead oxide and subtracting it from the total amount of oxide used, it was found that 2.4882 grams of normal potassium mucate reacted with 3.7854 grams of lead oxide. If one molecule of mucate reacts with two molecules of lead oxide, theory requires that 2.4882 grams of normal potassium mucate react with 3.8802 grams of lead oxide.

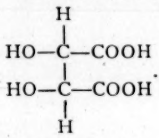
The white salt separated from the residual lead oxide was washed repeatedly with water, dried at 130° C. and analyzed. The granular salt was found free from potassium. 0.6863 gram of the substance dried at 130° C. in an atmosphere free from carbon dioxide yielded on evaporation with sulphuric acid, 0.7474 gram $PbSO_4$ = 0.5106 gram Pb = 74.4 per cent. The theory for $C_6H_4O_8Pb_2$ requires 75.27 per cent. It was consequently suspected that the salt dried at 130° still contained some water. However, on heating another sample it was found that at 133° the salt already began to turn yellow, showing that it could bear no further heating. In consequence, further work on the salt was suspended.

The basic lead saccharate and also the basic lead mucate here described have been known for some time. The basic lead

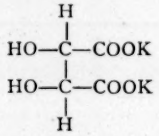
mucate was obtained by boiling mucic acid with basic lead acetate.[1] The basic lead saccharate was prepared by the same method as the mucate, and also by boiling lead oxide with the normal potassium salt of saccharic acid. The latter method was used by Hess.[2] It is the same as that above described.

Part II.—General and Theoretical.

The generally accepted formula for tartaric acid is



When its aqueous solution, either weak or concentrated, is boiled with metallic lead or lead oxide, very little or no reaction takes place. It has been shown above, however, that when its normal potassium salt, which has the formula



is treated with lead oxide, one molecule of the tartrate readily takes up one molecule of oxide. More than one molecule of oxide to one of tartrate may be taken up, but only with great difficulty, as after six hours' boiling the proportion was found to be only 1.2341 molecules of the oxide to one of the salt.

In view of the nature of tartaric acid on the one hand, and the peculiar character of lead on the other—lead being at once a strong base and also capable of performing the functions of an acid, as in the case of plumbites and plumbates—one would be inclined to think that when normal potassium tartrate and lead oxide react, molecule for molecule, the lead atom would replace

[1] Krug: Jsb. Chem. 1861, 368; see also Hagen: Ann. Chem. (Liebig) **64**, 349.
[2] *Ibid.* **30**, 306; see also Thaulow, *Ibid.* **27**, 113.

the two hydrogens of the alcoholic hydroxyl groups of the tartaric acid. But this is not in accord with the experimental evidence. It has been shown that when a solution of normal potassium tartrate is treated with lead oxide the resulting fluid is strongly alkaline—a fact due to the formation of caustic potash. Further, it is known that when one molecule of lead oxide reacts with one molecule of potassium tartrate the resulting alkalinity corresponds to one-half the potassium of the normal tartrate, or we may say that it is equivalent to one-half the lead. In general, no matter how much lead oxide is dissolved in a solution of normal potassium tartrate, the resulting alkalinity is equivalent to one-half the lead introduced.

From these facts it appears that when lead oxide acts, molecule for molecule, on potassium tartrate, one atom of potassium is replaced by the lead. When more than one molecule of lead oxide acts on one molecule of tartrate, one atom of potassium is replaced, and then the action goes on replacing the other atom of potassium; but this second step proceeds with much greater difficulty because of the modification the compound has undergone by the introduction of the first atom of lead. It may be possible to set free as hydroxide all the potassium of the tartrate by heating with excess of lead oxide under pressure, but up to the present, only a small fraction of the second half of the potassium has been set free.

That potassium hydroxide is set free by the lead has been established. On the other hand, it is evident that when potassium hydroxide acts on lead tartrate, the lead is partly crowded out of its place by the potassium. When the point of equilibrium is reached where the solution contains one atom of lead to two atoms of potassium to one molecule of tartaric acid, one atom of potassium and one atom of lead are held by the tartaric acid and the other atom of potassium is set free as hydroxide.

The behavior of acid potassium tartrate toward lead oxide ought, perhaps, to be briefly mentioned here. Acid potassium tartrate acts on lead oxide like ethyl potassium tartrate (see above), only much more slowly. The action of acid potassium tartrate is much aided by adding another half-molecule of potassium hydroxide to the mixture. The lead thus goes into solution; and at the point where one molecule of lead oxide has been taken up, the additional half-molecule of potassium hydroxide is present as such in the solution as determined by titration.

It was found that potassium malate acts with about as great difficulty on lead oxide as potassium tartrate does after one atom of lead has been introduced. The same is true of potassium citrate. The potassium salt of succinic acid, which contains no alcoholic hydroxyl groups, does not act on lead oxide. The reason for this behavior must be sought in the nature of the respective acids.

It has been shown that one molecule of potassium mucate reacts with two molecules of lead oxide, and that from the products of the reaction a very basic lead salt can be isolated. The same is true of potassium saccharate. That in these reactions lead also sets free potassium as hydroxide, there can be little room for doubt.

As it has been shown that of the number of acids tested, only the normal salts of tartaric, mucic and saccharic acids react with lead oxide, and as potassium tartrate reacts readily only with one molecule of lead oxide, and the salts of the other two acids react each with two molecules of lead oxide, we are led to the following conclusion: In order that its normal potassium salt may react readily with lead oxide, an organic acid must be bibasic and must contain two, or a multiple of two, alcoholic hydroxyl groups. Further, the number of molecules of the oxide with which one molecule of the salt readily reacts is equal to one-half the number of alcoholic hydroxyl groups the acid contains. Whether these statements will hold true in all cases must be further tested. The potassium salt of tri-oxyglutaric acid would afford a means for testing the correctness of these statements.

Summary of Results.

In the foregoing pages it has been shown that:

1. Normal potassium tartrate in aqueous solution dissolves a quantity of lead monoxide equivalent to one molecule for every molecule of tartrate, and an additional one-fourth molecule can be dissolved by long-continued boiling in very concentrated solution.

2. The solution of lead oxide in potassium tartrate has a strong alkalinity due to the formation of caustic potash.

3. From the solution of lead oxide in potassium tartrate a tribasic lead tartrate can be isolated.

4. The same solution is obtained whether lead oxide is dissolved in potassium tartrate or lead tartrate is dissolved in potassium hydroxide, provided that the same amounts of lead, potassium and tartaric acid are used in each case.

5. The normal tartrates of sodium, lithium and rubidium act like potassium tartrate toward lead oxide.

6. Lead monoxide is apparently the only oxide that will readily dissolve in potassium tartrate.

7. As far as tested, aqueous solutions of normal alkali salts of organic acids other than tartaric, mucic and saccharic react very slightly, or not at all, with lead monoxide.

8. The normal potassium salts of mucic and saccharic acids react each with a quantity of lead monoxide equivalent to two molecules to every molecule of salt, and from the products of the reactions a tribasic lead mucate and a tribasic lead saccharate, respectively, can be isolated.

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Contribution from the Laboratory of Wabash College.

ON TWO STEREO-ISOMERIC HYDRAZONES OF BENZOÏN.

BY ALEX. SMITH AND J. H. RANSOM.

The number of cases in which stereo-isomerism has been discovered to exist among the hydrazones is at present very limited. On this account it may be well to mention those in which such isomerism has been established with some approach to certainty.

The earliest with which we are acquainted is the preparation by Z. H. Skraup,[1] four years ago, of two monophenylhydrazones of grape-sugar, melting respectively at 144°–145° and 115°–116°. Fehrlin[2] found that the phenylhydrazone of orthonitrophenylglyoxylic acid (melting-point 165°–166°) could be transformed by

[1] Monatsh. Chem. **10**, 406; Ber. d. chem. Ges. **22**, 669 c.
[2] *Ibid.* **23**, 1574; see also Krause: *Ibid.* **23**, 3617.

the action of alcoholic caustic potash into an isomer melting at 189°–190°. Hantzsch and Kraft[1] obtained two isomers, melting respectively at 90° and 132°, by the action of phenylhydrazine on anisylphenylketone chloride. The ketone itself yielded the one with the higher melting-point alone. Markwald[2] describes two isomeric diphenylthiosemicarbazides which contain the same group as the hydrazones, and whose isomerism is therefore probably referable to the same cause. Finally, Hantzsch and Overton[3] have re-examined the case of anisylphenylketone and have prepared two isomeric hydrazones by the action of diphenylhydrazine, where all possibility of chemical isomerism seems to be excluded, and have further made the corresponding bodies from paratolylphenylketone.

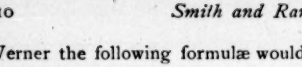
In all these cases the isomer with the higher melting-point is very stable, and can only be transformed into the less stable variety to a very small extent, if at all. That with the lower melting-point is easily decomposed into tarry products, and can frequently be converted into that with the higher melting-point. The first, called by Hantzsch the α-form, is much less soluble in ordinary solvents than the second, β-variety.

The authors had occasion to prepare benzoïn monophenylhydrazone in connection with another investigation, and the accidental discovery that two substances are formed of identical chemical composition, but differing considerably in melting-point, led them to investigate the action of phenylhydrazine on benzoïn under various conditions, and the properties of these derivatives in particular.

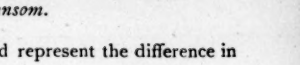
Obviously the occurrence of stereo-isomerism was possible, as the group , which was the common feature of previously described cases, was present here also. It soon became evident that the two bodies were really stereo-isomeric hydrazones, a fact which was the more interesting because both could be prepared directly from benzoïn, whereas with all the other stereo-isomeric hydrazones, one of the forms could only be prepared indirectly—from the ketone chloride, or by transformation from the other. According to the theory of Hantzsch and

[1] Ber. d. chem. Ges. **24**, 3525. [2] *Ibid.* **25**, 3099. [3] *Ibid.* **26**, 9 and 18.

Werner the following formulæ would represent the difference in structure:

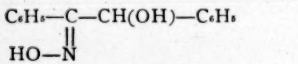


Stable; m.-p. 158°–159°. α-Hydrazone.

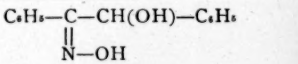


Unstable; m.-p. 106°. β-Hydrazone.

These would therefore correspond to Werner's[1] two isomeric oximes:



Stable; m.-p. 151°. α-Benzoïn-oxime.



Unstable; m.-p. 99°. β-Benzoïn-oxime.

Lackowicz[2] has recently made the anilide of benzoïn, but failed to find any evidence of isomerism.

Classing the modes of comparison of stereo-isomeric hydrazones and oximes under five heads, the following is a summary of the results obtained in this case:

1. In appearance the isomers resemble each other closely, but in the other physical characters there is a difference in degree. The melting-points show a difference of 52°–53°, which corresponds exactly with the difference of 52° in the case of the oximes. The β-modification is much more soluble than the α-modification; in the case of absolute alcohol the ratio is 4 : 1. In all its relations the former is also much less stable than the latter.

2. The substances are identical in chemical composition, molecular weight and mode of preparation, so that identity in chemical constitution is probable. This is confirmed by investigations under succeeding heads.

3. The action of some reagents is the same with both. For example, both are insoluble in dilute mineral acids. Both are converted into the diphenylhydrazone of benzil (melting-point 225°), by the action of excess of phenylhydrazine in acetic-acid solution. When heated with benzaldehyde, water is given off and both yield a substance melting at 215°–216°.

4. In the case of the oximes, the α- and β-modifications yield methyl, benzyl and other ethers by substitution, and give also

[1] Ber. d. chem. Ges. **23**, 2333.

[2] Monatsh. Chem. **14**, 279.

salts with hydrochloric acid, which always occur in two forms, so that each retains the space-configuration of the form from which it was made. In the case of phenylhydrazones there is no way known of preparing such derivatives readily, so that this method has not yet been applied to them.

5. Each modification can frequently be transformed into the other, or at all events the less stable one can be converted into the more stable. The latter was accomplished in the present case, after many unsuccessful attempts, by heating the β-hydrazone with two molecules of phenylhydrazine in alcoholic solution for several hours. An excellent yield of the α-variety was obtained in a pure condition.

Action of Phenylhydrazine in Acetic-acid Solution.—When benzoïn is dissolved in acetic acid, and boiled for half an hour with excess of phenylhydrazine, yellow needles are deposited as it cools. After recrystallization from acetic acid and benzene they melt at 225°, and are identical with the phenylhydrazone of benzil. They are formed, therefore, in the same way as the "osazones" of other 1.2 ketols.

0.1904 gram substance gave 24 cc. N at 20.5° and 746 mm.

	Calculated for $C_{28}H_{22}N_4$.	Found.
N	14.36	14.41

Action of one molecule of Phenylhydrazine on Benzoïn in Alcoholic Solution.—The interaction of the two substances was investigated by Pickel,[1] and later by Vogtheer.[2] Both of these observers obtained a monophenylhydrazone to which they assigned the melting-point 155°, as sole product. It was found that when their method was followed exactly, the alcohol being distilled off after prolonged heating, the resulting oil dissolved in benzene and light petroleum-oil added to the mixture, crystals are deposited abundantly which contain nothing but the substances described. If, however, the mixture of phenylhydrazine and benzoïn, in alcohol, after being heated on the water-bath for 3 to 4 hours, is allowed to cool, crystals are deposited which contain a variable proportion of a new substance melting at 106°,[3] mixed with the other product. A

[1] Ann. Chem. (Liebig) **232**, 229. [2] Ber. d. chem. Ges. **25**, 637.

[3] As the phenylhydrazone of desoxybenzoïn is stated by Ney (Ber. d. chem. Ges. **21**, 2447) to melt at 106°, this substance was prepared for comparison. The substance obtained by the action of phenylhydrazine on desoxybenzoïn melted, however, at 116°, but agreed otherwise with the description. The figure given and quoted in Beilstein (*Org. Chem.* **3**, 989) must therefore be a misprint for 116°.

microscopic examination of the crystals deposited from a drop of the alcoholic solution, by Lehmann's method,[1] showed the presence of two substances crystallizing in thin and thick prisms respectively, one of which melted before the other was affected by the heat of a small flame below the stage of the instrument. They may be separated by dissolving the crystalline mass in boiling light petroleum-oil. The lower melting substance first comes out in the form of large monoclinic prisms. As soon as the smaller needles of the higher melting substance begin to appear, the liquid is decanted. By repeating this process several times each substance is obtained free from the other. They now melt at 106° and 158°–159°, respectively. Subsequent experiments showed that the former is decomposed by prolonged heating with alcohol, and cannot be obtained crystalline after such treatment. The method of preparing the latter used by Pickel, therefore, prevented his finding the isomer.

As this method of separation was very laborious and led to much loss of material, conditions were sought under which the substances could be obtained separately. This was attained in two ways.

Preparation of the β-Monophenylhydrazone.—Benzoïn (20 grams) and phenylhydrazine (10 grams) are dissolved in 95-per cent. alcohol (200 cc.), warmed on the water-bath for three to four hours, and then set aside for twelve hours. At the end of that time a large amount of crystals will have deposited themselves, which, if the above conditions have been observed, will almost invariably consist of the β-monophenylhydrazone, and be quite free from the α-form. The filtrate from these crystals, on being shaken for a few seconds, deposits the α-form entirely free from any admixture of the β-form. The substances are recrystallized from alcohol, in which they are freely soluble.

If the β-hydrazone alone is required, it may be prepared more easily by cautiously heating molecular quantities of phenylhydrazine and benzoïn without any solvent, for two or three minutes over the naked flame. The reaction is complete when bubbles of steam have almost ceased to arise. The resulting thick oil is dissolved in alcohol, and an almost quantitative yield of the β-hydrazone is obtained. Only a few large crystals of the α-variety are sometimes found in the third or fourth crop of crystals.

[1] Lehmann: "Die Krystallanalyse" (Leipzig, 1891).

The following results were obtained on analyzing the two substances: The *α*-hydrazone was analyzed completely by Pickel, so that a nitrogen-estimation was considered sufficient.

α-Hydrazone; melting-point 158°–159°.

0.3882 gram substance gave 32.4 cc. N at 19° C. and 741.5 mm.

	Calculated for $C_{20}H_{18}N_2O$.	Found.
N	9.27	9.56

β-Hydrazone; melting-point 106°.

I. 0.2205 gram substance gave 0.6412 gram CO_2 and 0.1223 gram H_2O.

II. 0.3046 gram substance gave 0.8878 gram CO_2 and 0.1626 gram H_2O.

III. 0.2476 gram substance gave 20.7 cc. N at 24° C. and 747 mm.

		Found.		
	Calculated for $C_{20}H_{18}N_2O$.	I.	II.	III.
C	79.47	79.31	79.49	...
H	5.96	6.15	5.93	...
N	9.27	...	...	9.42

In physical properties there is a general resemblance between the two substances. Both consist of small white needles, which when pure do not change color on exposure to the air or sunlight. Both are soluble in warm light petroleum-oil, more soluble in warm alcohol, and very soluble in benzene. Both dissolve freely in warm acetic acid, but the *β*-variety does not reappear from the solution in crystalline form. Evaporation of the solution leaves a non-crystallizable oil. Even dissolving in alcohol seems to decompose some of the *β*-variety and render it oily, while the *α*-variety is quite unaffected by prolonged heating with alcohol. The *β*-variety is much more soluble in all these solvents than the isomer. Both substances are insoluble in alkalies and in dilute mineral acids. Strong hydrochloric and nitric acids convert them at once into tarry products. Concentrated sulphuric acid dissolves them with deep red coloration, which turns into a green on the addition of a crystal of potassium bichromate. Both reduce Fehling's solution on warming.

Leading dry hydrochloric-acid gas into alcoholic solutions of the hydrazones has in other cases led to the recovery of the ketone and phenylhydrazine hydrochloride. In the present case, how-

ever, the fact that hydrochloric acid acts on benzoïn itself doubtless explains the fact that only tarry products were obtained.

Molecular Weights of the Isomers.—As there was a possibility that the isomerism might be due to polymerization, the molecular weights of the isomers were determined by Raoult's method in benzene solution.

α-Hydrazone: 0.1972 gram, dissolved in 29.67 grams of benzene, lowered the freezing-point 0.12° C.; molecular weight = 277.

β-Hydrazone: 0.1337 gram, dissolved in 26.043 grams benzene, lowered the freezing-point 0.09° C.; molecular weight = 279.

Calculated molecular weight = 302.

Relative Solubility of the Hydrazones.—The relative solubility of the α- and β-hydrazones in absolute alcohol (Kahlbaum's) at 20° C. was measured by V. Meyer's method and was found to be in the ratio of 1 : 4.

α-Hydrazone: 0.0887 gram was found in 4.3768 grams of solution; solubility = 2.2 per cent.

β-Hydrazone: 0.4518 gram was found in 5.1032 grams of solution; solubility = 8.8 per cent.

Action of Benzaldehyde on both Hydrazones.—One molecule of benzaldehyde was cautiously heated with two molecules of the hydrazone in the naked flame for a few minutes. Water-vapor came off in considerable quantity, and on cooling, the thick oil solidified to a crystalline mass. On recrystallization from glacial acetic acid, in which the substance is somewhat soluble, small white plates were obtained which melted at 215°–216°. Both hydrazones yielded the same product. A determination of the nitrogen gave the following results:

0.3213 gram substance gave 24.5 cc. N at 24.5° C. and 739 mm.

	Calculated for $C_{47}H_{38}N_4$.	Found.
N	8.54	8.53

The substance was probably formed according to the equation $2C_{30}H_{18}N_2O + C_6H_5COH = C_{47}H_{36}N_4 + 3H_2O$.

It was only sparingly soluble in boiling alcohol and ether, and soluble in cold benzene. It did not reduce Fehling's solution, and no odor of benzaldehyde was perceptible on boiling it with dilute mineral acids. The establishment of the fact that both hydrazones produced it with equal ease was sufficient for the present purpose, and the substance has not yet been further investigated.

Formation of Benzil diphenylhydrazone from both Hydrazones.—It was expected that by the action of phenylhydrazine on the hydrazones, two of the three possible stereo-isomeric diphenylhydrazones of benzil would be obtained. On boiling them, however, with excess of phenylhydrazine in acetic-acid solution for half an hour, fine needles appeared in each case, which, after recrystallization from benzene, melted at 225° and were identical with the dihydrazone already known. From experiments presently to be described, it seems probable that this is derived from the α-monophenylhydrazone, and that when the β-monophenylhydrazone was treated as described, conversion into the more stable form preceded or accompanied the introduction of the second phenylhydrazo group.

Transformation of the β- into the α-modification.—Numerous experiments were made with this object in view. In the first place, each modification was subjected to prolonged boiling in alcoholic solution. The α-variety was entirely unaffected by this treatment, while the β-variety was largely converted into an uncrystallizable oil. The few crystals obtainable consisted of the original substance unchanged. Allowing the substances to stand in solution of alcoholic caustic potash for several hours had no effect except the partial decomposition of the less stable modification. Acetyl chloride converted both into tarry products.[1] The transformation was finally attained by boiling two molecules of phenylhydrazine with one molecule of the β-hydrazone in alcoholic solution for several hours. On cooling, the reddish-colored solution deposited fine white needles which consisted entirely of the α-hydrazone.

1 gram of the β-hydrazone gave 0.5 gram of the α-hydrazone.

Since the β-hydrazone is formed by fusion of the constituents, it seemed possible that heating the α-hydrazone for some time to a temperature slightly above its melting-point might produce the opposite transformation. Experiment showed, however, that beyond the production of a small proportion of oily material, the hydrazone is not altered by this treatment.

CRAWFORDSVILLE, INDIANA, *December* 7, 1893.

[1] When the β-modification was dissolved in acetyl chloride, and the excess of the latter allowed to evaporate *in vacuo* over sulphuric acid, the resulting oil seemed to be composed of an addition-product containing two molecules of acetyl chloride for each one of the hydrazone. 0.5601 gram of the hydrazone gave 0.8270 gram of the addition-product, while the theory demanded 0.8494 gram. No crystalline substance could be isolated, however.

ON THE ACTION OF BENZENESULPHONIC ACID UPON POTASSIUM IODIDE.—A NEW CLASS OF ORGANIC PERIODIDES.

By J. H. Kastle and Herbert H. Hill.

In view of the many interesting secondary reactions which take place when sulphuric acid is brought together with potassium iodide, it occurred to one of us (K.) that it might not be without interest to study the action of sulphonic acids upon this and other iodides.

In consequence of the ease with which it can be obtained, benzenesulphonic acid was chosen as the substance with which to make a few trial-experiments along this line; and acting upon our suggestion, Mr. Paul Murrill brought into solution in a small quantity of water small quantities of this acid and potassium iodide in equimolecular proportions. This solution, after having been heated for a time under an inverted condenser, became deep red-brown in color, indicating that some reduction had taken place and that iodine had been liberated. Upon cooling, a small quantity of a black crystalline substance, at the time mistaken for iodine, was deposited in the flask. Apparently the results obtained were not of sufficient interest to warrant further study; other matters of seemingly greater importance were awaiting our attention, and the flask containing the small quantity of black crystals was set aside. After standing for about two months it was observed that the solution had become filled with crystals, and upon pouring off the supernatant fluid there remained in the flask an aggregate of beautiful opaque crystals, green by reflected light and of a metallic luster, and strikingly different from iodine, with which they were at first confused. The crystals were removed from the flask and dried as rapidly as possible upon blotting-paper, and in order to remove the last traces of water were placed for a short while in a desiccator.

The substance thus obtained was found to dissolve rather freely in water, with the production of a deep reddish-brown color closely resembling that of a solution of iodine in potassium iodide. Upon boiling such a solution it was found that it lost its color

completely, large quantities of iodine escaping during the boiling; the clear solution thus obtained was found, however, still to contain notable quantities of iodine in the condition of an iodide. Upon analysis the following numbers were obtained:

	Found.	I. Calculated for $(C_6H_5SO_3K)_4.I_6$.	II. Calculated for $(C_6H_5SO_3K)_6.I_5$.
K	12.75	12.74	12.11
S	9.87	10.44	9.92
I (fixed)[1]	6.27	...	...
I (loosely held)	33.70	...	...
I (total)	39.97	41.31	39.26

	Found.	III. Calculated for $C_6H_5SO_3K.I_3$.	IV. Calculated for $(C_6H_5SO_3K)_3.KI.I_5$.
K	12.75	13.8	13.18
S	9.87	9.42	8.99
I (fixed)[1]	6.27	...	7.12
I (loosely held)	33.70	...	35.60
I (total)	39.97	44.73	42.72

In consequence of the high percentage of iodine Formula III is certainly to be rejected. It is not, however, without some misgiving that one selects either of Formulas I, II and IV as correctly representing the composition and nature of the compound obtained in the manner above described. This is especially true in that, so far as we have been able to discover, there is nothing in the literature which throws any side-light upon the nature of each as a compound unless it be the studies of Jörgensen, Dittmar, Ostermayer, Tilden, and others upon the periodides of the alkaloids and certain organic bases; and even here there is nothing to indicate any very close relationship or analogy beyond the fact that both classes of derivatives are organic and that both partake of the nature of periodides—in fact, looked at from any other standpoint, they are certainly widely different, it might almost be said opposite.

So far as the mere numerical argument is concerned between the results of the analysis and the percentages calculated for the

[1] By the "fixed" iodine is here meant that portion of this element which is not removed from the compound by boiling with water; while by the term "loosely held" is meant that portion which is thus easily removed.

several formulas above given, it will be seen that the agreement is rather more close with Formula II than with either of the others. This formula, however, fails to give expression to one of the most fundamental properties of the compound—that is, its partial decomposition by boiling water, and even by heat alone, by virtue of which it loses five-sixths of its iodine, the other one-sixth being held behind in the resulting compound or mixture in the condition of an iodide.

Formula I is open to the same objection.

Formula IV, $(C_6H_5SO_3K)_5.KI.I_5$, however, has been found to agree reasonably well with the results of analysis and the general properties of the compound. Comparing it with the analytical results above given, it will be observed that the greatest difference exists between the found and calculated percentages of iodine. This difference is probably to be accounted for by the fact that the compound continually gives off small quantities of iodine even at ordinary temperatures. In its relation to the observed properties of the compound it will be seen that this formula accounts in some measure for the decomposition of the compound by means of boiling water and by heat alone. It indicates that one-sixth of the iodine exists in the compound in intimate combination as an iodide; and that the remaining five-sixths sustain to the molecule a somewhat different relation and, it may be, are more loosely held. This formula suggests that the compound in question is a kind of mixed salt, and that it is a periodide as well; and—of still greater import—it points the way to a simple method for the preparation of the substance, the success or failure of which may be regarded, in some measure at least, as proof or disproof of the correctness of the views embodied therein.

The formula $(C_6H_5SO_3K)_5.KI.I_5$ indicates of course that the substance may be prepared by bringing together potassium benzenesulphonate, potassium iodide, and iodine.

Potassium Benzenesulphon-periodide,[1] $(C_6H_5SO_3K)_5.KI.I_5$.—Acting upon the above suggestion, a small quantity of potassium benzenesulphonate was dissolved in the smallest quantity of water in which it would dissolve; the required quantity of iodine was

[1] Concerning the nomenclature of the salts we have been somewhat at a loss. It would perhaps be better to call the compounds "Periodo-sulphonates," were it not for the fact that this name might lead to confusing these compounds with the iodine substitution-products of the sulphonic acids.

then got into solution in a small quantity of water by the aid of somewhat more potassium iodide than that required by the theory, and the two solutions thus obtained were mixed together. A heavy crystalline precipitate at once made its appearance. This was then made to dissolve in its own mother-liquor by the aid of a little water, and the solution thus obtained set aside to crystallize. This it did after some days. From time to time several crops of crystals were removed one after the other from the solution, and so far as could be determined there was no difference either in the appearance or composition of the several crops. The crystals thus obtained are thin, much elongated, rectangular prisms. They are opaque, but have a brilliant, greenish bronze-like luster by reflected light. When observed in the solution or when first removed they are exceedingly beautiful, but after drying, and especially after long standing in the open air or even in a closed tube, they lose something of their brilliant luster and even become, in some instances at least, partially covered over by a deep brownish coating. The odor of iodine is at all times perceptible about the crystals, even after they have been thoroughly dried, and this slow loss of iodine probably accounts for the change in appearance which they gradually undergo.

Analyses were made of several of these different crops with the following results:

	I.	II.	III.	IV.	Calculated for $(C_6H_5SO_3K)_3.KI.I_3$.
K	12.77	12.89	...	...	13.18
S	9.21	9.87	...	9.18	8.99
I (fixed)	6.7	7.	...	7.8	7.12
I (loosely held)	33.7	34.95	...	34.11	35.60
I (total)	40.4	41.91	42.16	41.91	42.72

The sulphur and potassium were determined in the above analyses by the usual methods; the "fixed" iodine by boiling a weighed portion of the compound with water until completely decolorized, and then titrating with $\frac{1}{10}$-normal silver-nitrate solution.

The "loosely held" iodine was determined directly with a standard solution of sodium thiosulphate, and the total iodine by treating a weighed portion of the compound with a small quantity of water and zinc-dust, filtering and titrating the filtrate with $\frac{1}{10}$-normal silver nitrate.

In some respects the results of these analyses are not as good as might be desired. It must be borne in mind, however, that the compound loses iodine rather readily and, farther, that no attempts were made to recrystallize the substance. In view of the method used in the preparation of the substance, and its decomposition by boiling water, there is little room for doubt that the composition and, in some respects, the structure of this substance, are correctly represented by the formula above given.

Sodium Benzenesulphon-periodide, $(C_6H_5SO_3Na)_5.NaI.I_4$.—The composition and character of the potassium compound naturally suggest that a corresponding sodium salt is possible. This salt was made by a method strictly analogous to that already given for the potassium salt. 9 grams of sodium benzenesulphonate were dissolved in 100 cc. of water, and to this was added a solution of 10 grams sodium iodide and 7 grams of iodine in 100 cc. of water, and the mixed solution allowed to stand. Under these conditions a sodium salt crystallized out which was found to resemble the potassium compound in almost every particular. It crystallizes in opaque acicular crystals of a bronze-green color and luster by reflected light. The substance is freely soluble in cold water, and is decomposed by boiling water, with the separation of the greater part of the iodine. It is also decomposed by heat alone, iodine being evolved, and, like those of the potassium salt, the dry crystals slowly lose a portion of their iodine at the ordinary temperature when exposed to the air.

The substance was analyzed with the following results:

	I.	II. Calculated for	III.
	Found. $(C_6H_5SO_3Na).I.$	$(C_6H_5SO_3Na)_5.NaI.I_3.$	$(C_6H_5SO_3Na)_5.NaI.I_4.$
Na	8.3	7.51	8.21	8.8
S	11.05	10.44	9.51	10.28
I (fixed)	8.04	...	7.53	8.14
I (loosely held)	31.17	...	37.65	32.57
I (total)	39.21	41.32	45.18	40.71

Taking everything into consideration, Formula III agrees best with the composition and properties of this compound. The ratio between the "fixed" iodine and that in the periodide condition is undoubtedly greater than that found to exist in the potassium salt. Concerning this difference of composition it may be that a series of these mixed salts is possible, such as the following:

$(C_6H_5.SO_3M)_6.MI$;
$(C_6H_5.SO_3M)_6.MI.I$;
$(C_6H_5.SO_3M)_6.MI.I_3$;
$(C_6H_5.SO_3M)_6.MI.I_5$;
$(C_6H_5.SO_3M)_6.MI.I_4$;
$(C_6H_5.SO_3M)_6.MI.I_6$; *etc., etc.;*

and that the potassium and sodium compounds which have already been described really represent two different members of such a series. In this connection it might not be amiss perhaps to call attention to the fact that among the periodides of certain of the alkaloid bases—the only compounds, so far as we have been able to discover, which in any way bear a relation to the compounds under investigation—such a series has been found to exist. Jörgensen, who has made a careful study of this whole subject, distinguishes seven compounds of quinine, sulphuric acid, and iodine, four of which belong to the herapathite type. Letting Q stand for the molecule of quinine, $C_{20}H_{24}N_2O_2$, the series stands as follows:

$4Q.3H_2SO_4.2HI.I_4$
$4Q.3H_2SO_4.2HI.I_5$
$4Q.3H_2SO_4.2HI.I_6$
$4Q.3H_2SO_4.2HI.I_7$

Barium Benzenesulphon-periodide, $[(C_6H_5SO_3)_2Ba]_6.BaI_2.I_{10}$.—This compound was obtained by a method exactly similar to those already given under the description of the potassium and sodium salts. A saturated solution of barium benzenesulphonate was added to one of the required quantity of iodine and enough barium iodide to hold it in solution, when the barium salt was precipitated as a crystalline, bronze-green precipitate. This was then got into solution in its own mother-liquor by the addition of more water and the solution allowed to stand. After a time the substance made its appearance in the liquid in the form of fine needle-shaped crystals, having the characteristic greenish-bronze color and luster by reflected light.

Up to the present the substance has been obtained only in small quantity, and hence has not been studied as closely as either of the substances described above; a barium determination was made, however, with results which agree fairly well with the formula above given:

	Found.	Calculated for $[(C_6H_5SO_3)_2.Ba]_6.BaI_2.I_{10}$.
Ba	20.55	20.99

The attempt was also made to prepare the corresponding calcium salt. The constituents of the salt were brought together in water and the solution placed under a desiccator. After standing for a time, a brownish-red substance made its appearance, altogether unlike any of the substances obtained in this investigation. The substance was evidently impure and was not further examined. The dish was then allowed to remain under the desiccator until all of the water had been absorbed, and there was left behind in the bottom of the dish a crystalline residue having the general appearance of the salts already described; it was so admixed with impurities, however, that no analysis of the compound was attempted.

As stated in the opening paragraphs of this paper, this study was first undertaken with the view to determine the action of the sulphonic acids upon potassium iodide, and while we have been diverted from our original purpose by the study of this new and interesting class of derivatives obtained at the outset, it has not been lost sight of. From the facts at present at hand it would seem that the benzenesulphonic acid acts upon the potassium iodide with the production of potassium benzenesulphonate and hydriodic acid, and that then the hydriodic acid reduces a part of the benzenesulphonic acid to benzenesulphinic acid, with liberation of iodide, which in turn combines with some of the potassium benzenesulphonate and potassium iodide to form the compound which for lack of a better name we have called potassium benzenesulphon-periodide.

It will be remembered that in the original experiment the benzenesulphonic acid and potassium iodide were brought together in aqueous solution, and it can easily be conceived that possibly other and highly interesting reactions may take place in more dilute or more concentrated solutions, or especially if the pure, dry acid be heated with the potassium iodide.

It is our purpose to make a more complete study of this reaction than has been possible thus far. Other sulphonic acids are even now in the course of preparation, with the view to making iodine derivatives similar to those described above, in the hope that among a great number of such compounds some few at least will be found which will throw more light upon the nature of the whole class.

STATE COLLEGE OF KENTUCKY, LEXINGTON, *January* 1, 1894.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON DIAMIDOORTHOPHOSPHORIC AND DIAMIDOTRIHYDROXYLPHOSPHORIC ACIDS.

By H. N. Stokes.

The highest hydrate of phosphorus pentoxide, pentahydroxylphosphoric acid, $P(OH)_5$, as is well known, has not yet been obtained, and it is extremely questionable whether it is capable of existence under ordinary conditions. Although no salts or esters of this acid have been prepared, the probability of their existence is much greater, it being a general rule that salts and esters of polyhydroxyl acids are more stable than the acids themselves, if the hydroxyls are united to the same atom. A few basic phosphates are known, it is true, but these are to be regarded as true basic salts, not as derivatives of pentabasic phosphoric acid.

The object of this article is to describe two amidophosphoric acids, one of which is to be referred to the common orthophosphoric acid, and which may be named *diamidoorthophosphoric acid*, the other derivable from the hypothetical pentabasic acid, and which may be designated as *diamidotrihydroxylphosphoric acid*. The relation of these acids is shown in the following formulas:

$$PO(OH)_3,\ PO\overset{(NH_2)_2}{OH};\quad P(OH)_5,\ P\overset{(NH_2)_2}{(OH)_3}.$$

Like orthophosphoric acid, diamidoorthophosphoric acid exists in the free state. The free diamidotrihydroxyl acid is apparently incapable of existence, passing at once on liberation into the ortho compound. A well characterized series of salts has been prepared, however, which indicate that it is a pentabasic acid, the amide hydrogen being in part replaceable by metal.

In a recent article[1] I have described the preparation and properties of monamidoorthophosphoric acid. By an analogous process the diamido acid is obtained. Phenyldichlorphosphate[2] is converted by aqueous ammonia into phenyldiamidophosphate, $PO(NH_2)_2(OC_6H_5)$, a highly crystalline and stable body, which, on saponifying with alkali or baryta and acidifying with acetic

[1] This Journal 15, 198.

[2] I use the term *phenyldichlorphosphate* for $PO.Cl_2(OC_6H_5)$, in preference to the usual name phenylphosphoric dichloride, as being analogous to *phenyldiamidophosphate*. This, on the older system, should be named phenylphosphoric diamide.

acid, yields the free acid, which has the composition represented by $PN_3O_3H_6$. The direct product of saponification is unquestionably a salt of the trihydroxyl acid; from this, by loss of water, the free acid is formed. Its actual constitution may be represented by two formulas, according to the manner in which this occurs:

$$P\begin{matrix}(NH_2)_2\\(OH)_3\end{matrix} - H_2O = PO\begin{matrix}(NH_2)_2\\OH\end{matrix} \text{(a), or } PNH\begin{matrix}NH_2\\(OH)_2\end{matrix} \text{(b).}^1$$

Which of these corresponds to the acid obtained, or whether both forms can exist, cannot be decided with any certainty from present data. As the action of nitrous acid fails to indicate difference of function of the two nitrogen atoms, and in the absence of any experimental evidence of the contrary, I prefer to adopt (a) provisionally. One or two salts must, however, be referred to an acid having the constitution (b).

The properties of the acid may be here stated briefly, leaving a fuller description to the second or experimental part of the article. It is crystalline, and is more stable than monamidophosphoric acid; it has a sour taste and decomposes carbonates in the cold, forming primary salts. The salts of the alkalies and earths are extremely soluble and devoid of crystallizing power; the silver salts are the most characteristic; it forms salts with one, two, three, four and five atoms of silver, and double salts with silver and alkali metals. Some of these have characteristic colors, and with increasing amounts of silver show an increasing tendency to deflagrate or explode, that with five atoms detonating violently on gentle friction. Many of them are diamidotrihydroxylphosphates; those which are not (including alkali salts), add bases directly, forming salts of this acid. Primary silver diamidophosphate, for example, does not give silver oxide when treated with an excess of potassium hydroxide; the potash is added directly, forming a

[1] In order to distinguish possible isomers of these bodies, I propose to designate those containing the phosphoryl group, PO, as *phosphoric* compounds, and those in which the group P(NH) occurs as *phosphimic* compounds. The three forms derivable from orthophosphoric acid by substituting amide for hydroxyl, and their three isomers would then be:

$PO\begin{matrix}NH_2\\(OH)_2\end{matrix}$, monamidophosphoric acid; $P(NH)(OH)_3$, phosphimic acid.

$PO\begin{matrix}(NH_2)_2\\OH,\end{matrix}$ diamidophosphoric acid; $P(NH)\begin{matrix}NH_2\\OH,\end{matrix}$ amidophosphimic acid.

$PO(NH_2)_3$, phosphoryl triamide; $P(NH)\begin{matrix}(NH_2)_2\\OH,\end{matrix}$ diamidophosphimic acid.

As this nomenclature cannot be rigidly adhered to in the absence of more definite evidence as to the nature of these bodies, where there is no presumption in favor of one formula rather than the other, the terms amidophosphoric, etc., will be used.

colorless gelatinous salt, which is undoubtedly $POAg\begin{matrix}(NH_2)_2\\(OK)_2\end{matrix}$; from this, by transformations to be described later, the following series is obtained:

$(NH_2)_2$	$(NH_2)_2$	$(NHAg)_2$	$(NHAg)_2$
$P(OAg)_2$,	$P(OAg)_2$,	$P(OAg)_2$,	$P(OAg)_2$,
OK		OH	
White.	Yellow.	Red-brown.	Dark brown.

as well as several other bodies of uncertain composition. A secondary silver salt has also been obtained, which, in the dry state, is apparently $P(NH)(NH_2)(OAg)_2$, but which, in freshly precipitated and moist condition, acts like $P(OAg)_2\begin{matrix}(NH_2)_2\\OH\end{matrix}$, a derivative of the trihydroxyl acid. These salts are readily converted into each other or back into the original substance.

Diamidotrihydroxylphosphoric acid is therefore pentabasic, the amide hydrogen being readily replaceable by metal, the compounds thus formed showing no tendency whatever to decompose into oxide and salts of diamidoorthophosphoric acid. The formation of the salt $PN_2H_4O_5KAg_2$ in thirty per cent. caustic potash solution seems to indicate, however, that the amide hydrogen is not replaceable by alkali metals.

Diamidotrihydroxylphosphoric acid may be regarded as orthophosphoric acid in which the oxygen of the phosphoryl group is replaced by two amido groups:

$$O=P(OH)_3; \qquad (NH_2)_3=P(OH)_3.$$

The analogy appears in the yellow tertiary silver salt, which was at first mistaken for silver phosphate:

$$O=P(OAg)_3; \qquad (NH_2)_3=P(OAg)_3,$$

the yellow color being possibly due to the common chromophore $=P(OAg)_2$.

A further study of monamidophosphoric acid, now being made, shows that besides the white primary and secondary salts described,[1] others of yellow, red and brown color exist, which may possibly be referred to a monamidotetrahydroxylphosphoric acid.

[1] This Journal **15**, 211.

Phosphoryltriamide, if it can be obtained, will probably act in a similar manner, existing not only as $PO(NH_2)_3$, but in salts as triamidodihydroxylphosphoric acid, $P\overset{(NH_2)_2}{(OH)_2}$.

Experimental Part.

Phenyldiamidophosphate, $PO\overset{(NH_2)_2}{OC_6H_5}$.—1 mol. wt. phenol is boiled with somewhat more than 1 mol. wt. phosphorus oxychloride, until the evolution of hydrochloric acid ceases. The phenyldichlorphosphate, $PO.Cl_2.OC_6H_5$,[1] is approximately purified by two distillations, the portions passing over between 200°–300° being reserved. The product is poured, drop by drop, with constant stirring, into ammonia water of about sp. gr. 0.9, which is kept cool in ice,[2] 400 cc. ammonia being taken for 100 grams dichloride. The reaction is accompanied by a crackling noise, and separation of phenyldiamidophosphate as a pure white granular solid. This is readily filtered off by suction, washed a few times with cold water, dried on clay plates and recrystallized twice from a large volume of boiling 95-per cent. alcohol. The ammoniacal mother-liquor retains a small portion in solution, which cannot be recovered by evaporation. The yield of crude diamide is 45–55 per cent. of the theoretical, calculated from the amount of dichloride, or 30–35 per cent. of the amount theoretically obtainable from the phosphorus oxychloride used, a portion of this having been lost in the form of unchanged substance or of phenylphosphates. The rest of the dichloride is probably converted mostly into phenylphosphoric acid, but a small quantity of phenylamidophosphoric acid, $PO.NH_2.OH.OC_6H_5$[3] is formed, which may be separated by removing most of the ammonia by a strong current of air, neutralizing and precipitating by cupric sulphate. On decomposing the copper salt with sodium sulphide, saponifying the filtrate with caustic soda and adding acetic acid, the difficultly soluble primary sodium amidophosphate[4] is obtained, recognizable by its crystalline form and by conversion into other characteristic salts. The yield is not great.

Phenyldiamidophosphate is permanent in the air, and loses nothing at 100°. The analysis of two preparations gave:

[1] G. Jacobsen: Ber. d. chem. Ges. **8**, 1521. Boiling-point 241°-243°.
[2] Cooling with ice and salt does not increase the yield.
[3] This Journal **15**, 201. [4] *Ibid.* **15**, 204.

	Calculated for $PO.(NH_2)_3.OC_4H_5$.	Found. (1).		(2).
P	18.04	18.31		18.13
N	16.32	16.08	15.92	16.18

(1). P : N = 1 : 1.94 and 1.92. (2). P : N = 1 : 1.97.

Phosphorus was determined as magnesium pyrophosphate, after repeated evaporation with caustic soda and hydrochloric acid; nitrogen as ammonia, after boiling a quarter of an hour with dilute hydrochloric acid.

Phenyldiamidophosphate crystallizes from alcohol in brilliant colorless rhombic scales, or plates which seem to be monoclinic, and which in masses much resemble naphthalene. Cold water dissolves it but slightly, although much more readily than diphenylmonamidophosphate; it may be recrystallized unchanged from boiling water. It dissolves in about 100 parts cold and 10 parts boiling 95-per cent. alcohol; other neutral solvents dissolve it but very slightly. It fuses, but not sharply, at 185°–190°, undergoing partial decomposition, indicated by evolution of ammonia and falling of the melting-point; at a higher temperature it gives off ammonia and phenol, and leaves a white phosphatic residue. Dilute mineral acids dissolve it very slowly in the cold, readily on boiling, decomposing it into ammonia and phenylphosphoric acid; dilute and concentrated acetic acid, hot or cold, act as solvents merely, the glacial acid dissolving it quite readily. Caustic potash, soda, ammonia and baryta saponify it readily on boiling, giving salts of diamidophosphoric, or more probably, diamidotrihydroxylphosphoric acid; it is but slowly soluble in cold dilute alkali. The saponification is accompanied with scarcely any evolution of ammonia, unless in the case of extremely concentrated boiling solutions, when it may be regarded almost as a fusion. This is not to be reconciled with the opinion of Mente[1] that the non-appearance of ammonia is proof that the nitrogen in these compounds exists in the form of *imido* groups. The acid under consideration must contain at least one amido group, yet it is scarcely decomposed by alkali.

Action of Dry Ammonia on Phenyldichlorphosphate.

Hoping to obtain a better yield of phenyldiamidophosphate, phenyldichlorphosphate was subjected to the action of dry ammonia gas. The following reactions were expected:

[1] Ann. Chem. (Liebig) **248**, 240, 247.

$$(1).\ PO\begin{matrix}Cl_2\\OC_6H_5\end{matrix} + 2NH_3 = PO\begin{matrix}NH_2\\Cl\\OC_6H_5\end{matrix} + NH_4Cl.$$

$$(2).\ PO\begin{matrix}Cl_2\\OC_6H_5\end{matrix} + 4NH_3 = PO\begin{matrix}(NH_2)_2\\OC_6H_5\end{matrix} + 2NH_4Cl.$$

Calculated increase of weight in (1) 16.1 per cent., in (2) 32.2 per cent.

The temperature was at first kept down by immersing the flask in cold water. There resulted a semi-fluid mass with an increased weight of 14.7 per cent., which remained nearly unchanged after prolonged action at 100°. The product, covered with strong aqueous ammonia, became warm, but there was no strong reaction; it became thick and pasty, but did not solidify even after prolonged action. No diamide could be obtained from this by extraction with hot alcohol; had it been formed, it would certainly have been detected.

It might be concluded from the increase of weight observed that the dry ammonia had replaced only one-half of the chlorine by amide; this conclusion, however, is unjustifiable. Had the reaction taken place as in equation (1), aqueous ammonia would have generated some diamide. Moreover, other reactions could occur, requiring the same increase as equation (1), for example:

$$(3).\ 3PO\begin{matrix}Cl_2\\OC_6H_5\end{matrix} + 6NH_3 =$$
$$\left(PO\begin{matrix}Cl_2\\OC_6H_5\end{matrix}\right).NH.(PO.OC_6H_5).NH.\left(PO\begin{matrix}Cl_2\\OC_6H_5\end{matrix}\right) + 4NH_4Cl,$$

where the ratio of chloride to ammonia is also 1 : 2, yet two-thirds of the chlorine have been acted on. It is highly probable that the action of dry ammonia occurs in a sense analogous to equation (3), a mixture of more or less complex imidophosphates being produced. The reaction was not studied further.

Saponification of Phenyldiamidophosphate.

Diamidoorthophosphoric Acid, $PO\begin{matrix}(NH_2)_2\\OH\end{matrix}$.—On placing two or three molecular weights solid caustic potash on one molecular weight ether and adding a little cold water, the heat of solution of the alkali is sufficient to start the reaction, and the ether dissolves completely. The solution is boiled five minutes to make sure of complete decomposition. It is noteworthy that if

less than three molecular weights potash be used much phenol is liberated, but if the amount of potash equal three molecular weights all phenol is held in combination as phenylate; an indication that the salt in solution contains two atoms of potassium. The solution is cooled in ice and a little more than the calculated quantity of strong acetic acid added gradually, when the diamidophosphoric acid crystallizes out at once as a coarse white powder, which, under the microscope, is seen to consist of six-sided plates, united to pairs by overlapping or fusion at the angles. More may be obtained by adding five or six volumes of alcohol to the mother-liquor. It is then sucked out and washed with alcohol. It may be redissolved in water and reprecipitated by alcohol, but the analyses indicate that this does not result in a purer product. When precipitated by alcohol it usually forms ×-shaped skeleton plates, with parallel striations in the direction of the longer axis, or frequently large thick ×-shaped forms with dentate edges; other forms were occasionally observed. The yield is about 65 per cent. of the theoretical, the rest remaining in solution in the dilute alcohol, and separating but very slowly and imperfectly in impure form.

Whether prepared as above or by decomposition of the silver salt with sulphuretted hydrogen, it always evolves a small amount of ammonia on treatment with alkali in the cold, which does not increase on boiling, and hence is not due to direct decomposition, but probably to the presence of a little ammonium phosphate or monamidophosphate. This is indicated in the analyses, in which the phosphorus and nitrogen, but especially the latter, fall somewhat too low. All analyses were made with substance dried *in vacuo* over sulphuric acid.

	Calculated for $PO.(NH_2)_2.OH$.	Found. (1).	(2).
P	32.28	32.15	...
N	29.22	27.66, 27.66	28.10, 28.16, 28.10

	Found. (3a).	(3b).	(3c).	(4).
P	31.70	31.67	32.17	32.16
N	28.13	27.56	27.93	27.70

(1). P : N = 1 : 1.90. From acetate solution by alcohol, dissolved in water and reprecipitated by alcohol.

(2). Prepared like (1).

(3*a*). P : N = 1 : 1.96. Direct crystallization from acetate solution, without alcohol.

(3*b*). P : N = 1 : 1.97. From mother-liquor of (3*a*) by alcohol.

(3*c*). P : N = 1 : 1.92. (3*a*) dissolved and reprecipitated by alcohol.

(4). P : N = 1 : 1.90. From primary silver salt by sulphuretted hydrogen; precipitated by alcohol.

For analysis, the substance may be decomposed by boiling for ten or fifteen minutes with dilute hydrochloric or sulphuric acid; longer than this is useless, as the decomposition takes place easily. Concentrated sulphuric acid must not be used, as the action is violent.

The decomposition of the primary silver salt by sulphuretted hydrogen and precipitation by alcohol gives a good yield, and the acid shows the characteristic form.

Diamidoorthophosphoric acid is moderately soluble in cold water, and nearly insoluble in alcohol. It is permanent in the air, and loses nothing over sulphuric acid. At 100° it slowly fuses, undergoing a slight increase of weight, probably due to absorption of moisture, and is converted into ammonium salts of unknown nature, as it gives a copious white precipitate with silver nitrate, which is without action on the acid itself. At a higher temperature it gives off ammonia, and finally volatilizes without residue, attacking platinum. It is much more stable than monamidophosphoric acid, and apparently may be kept indefinitely without change. It also differs from the latter, which has a sweetish taste, in being decidedly sour. Its reaction towards litmus and methyl orange is acid, but no sharp end-reaction can be obtained with either indicator. It readily decomposes insoluble carbonates in the cold, apparently forming primary salts only. Boiling with moderately concentrated alkali liberates ammonia but very slowly after the small quantity due to impurity has been expelled. A weighed portion was boiled an hour with an excess of baryta, the ammonia being collected and determined; it corresponded to a decomposition into phosphoric acid of 4.5 per cent., but part of this was due to original contamination. This is in marked distinction from monamidophosphoric acid, which is instantly decomposed on boiling with excess of baryta,[1] although almost unacted on by boiling alkali.[2] Even the primary salts are quite slowly

[1] This Journal **15**, 206, 207. [2] *Ibid.* **15**, 203.

decomposed on boiling, and sometimes separate in nearly pure form from boiling solutions. The free acid, on the contrary, is rapidly destroyed by boiling water, with evolution of ammonia, but passes through at least two intermediate stages before being converted into phosphoric acid. Boiled for less than a minute and then cooled, the solution gives no precipitate with barium chloride, but a white curdy precipitate with silver nitrate, which melts under hot water to a transparent liquid, solidifying on cooling to a hard and often transparent glass, suggesting silver hexametaphosphate; it is not this, however, but the salt of a nitrogenous acid. If boiled for a minute or two, both barium chloride and silver nitrate give white precipitates, the latter turning yellow under boiling water, but not melting. These products have not been further examined. On longer boiling it gives ammonium phosphate.

Saponification by Ammonia.—The action of ammonia on the phenyl ether differs from that of the fixed alkalies. Diamidophosphoric acid is formed at first, but owing to the instability of the ammonium salts, these act more like the free acid or primary salts on boiling. After short boiling, the acid is formed which gives the easily fusible silver salt just referred to; on longer boiling (about an hour) this acid changes to another, the silver salt of which is white, amorphous, and infusible under boiling water; at the same time phosphoric acid is formed. On precipitating with silver nitrate, dissolving in ammonia and precipitating in fractions by nitric acid, a colorless salt was obtained, which gave on analysis P, 11.51; N, 3.87; Ag, 66.25, or P : N : Ag = 4 : 2.94 : 6.53. The substance was obviously a mixture, but the figures suggest a possible imido acid, having the same relation to tetraphosphoric acid as pyrimidophosphoric[1] does to pyrophosphoric acid.

Saponification by Baryta.—The action of baryta on diphenylmonoamidophosphate is to saponify readily one phenoxyl group only;[2] the second is attacked but slowly, and as fast as this occurs the barium amidophosphate decomposes. Markedly different is its behavior towards the diamido ether. One part ether is boiled for ten or fifteen minutes with 2 parts crystallized baryta and 10 parts water. There occurs a very slight evolution of ammonia and formation of a precipitate, but unless the boiling be long con-

[1] This Journal **15**, 212. [2] *Ibid.* 202.

tinued the decomposition is trifling. On cooling and treating with carbon dioxide, the primary salt remains in solution, and this affords the best starting material for preparing the silver salts below mentioned.

Action of Nitrous Acid on Diamidophosphoric Acid.

The action of nitrous acid on diamidophosphoric acid was studied, hoping to obtain some indication as to whether it has the constitution expressed by $PO\begin{matrix}(NH_2)_2\\OH\end{matrix}$ or by $PNH\begin{matrix}NH_2\\(OH)_2\end{matrix}$.

Primary diamidophosphates are without action on sodium nitrite, but the free diamidophosphoric acid decomposes it readily, nitrogen being given off in the cold, rapidly from concentrated, slowly from dilute solutions, and primary sodium monamidophosphate, which is difficultly soluble, crystallizes out. As the yield of the latter is considerably below the theoretical, it would seem that the liberated nitrous acid does not attack only one amido (or imido) group by preference, but that it acts indiscriminately, a mixture of primary phosphate, mono- and diamidophosphate resulting. These primary salts are not sufficiently acid to decompose any excess of sodium nitrite, and the reaction ceases here. If, however, a little acetic acid (which does not decompose the amidophosphoric acids) be added, more nitrous acid is liberated and decomposition to phosphate is complete. The latter is recognized, and found to be free from amidophosphates, by diluting largely and precipitating with ammonia and silver nitrate. There being no apparent difference in the ease with which the two nitrogen atoms are removed, there is no evidence in this direction of their having different functions.

The difficultly soluble sodium salt was purified by dissolving in caustic soda and precipitating by acetic acid, and then dissolved in ammonia together with two molecular weights silver nitrate, and precipitated by nitric acid. A white salt was obtained which gave on analysis figures corresponding to secondary silver monamidophosphate :[1]

	Calculated for $PO(NH_2)(OAg)_2$.	Found.
P	9.98	10.10
Ag	69.40	68.95

or P : Ag = 1 : 1.96.

[1] This Journal **15**, 211.

A peculiar difference was observed between the monamidophosphates made in the usual way (α series) and those prepared as above from diamidophosphoric acid (β series), and which was at first supposed to be due to their being derived from the isomeric forms $PO.NH_2(OH)_2$ and $PNH(OH)_3$. Primary sodium α-amidophosphate[1] crystallizes in unusually well formed hexagonal pyramids or prisms; the β-salt sometimes forms oblongs with rounded ends, sometimes circular disks, sometimes mulberry shapes, but always devoid of sharp angles even after several recrystallizations; both salts have apparently the same solubility. The secondary α-silver salt forms rhombic plates, or prisms; the β-salt, spherical aggregates of innumerable extremely fine needles, distinguishable only under a high power, and this form persists after recrystallization. In the case of several other salts the α- and β-compounds were of different crystalline habit, in others they were identical, though with a tendency on the part of the β-series to form smaller and less distinct crystals. The action of boiling water was identical. Equal weights of α- and β-sodium salts were then dissolved together in caustic soda and precipitated by an excess of acetic acid. If different, they would probably crystallize separately; if identical, the difference being due to impurity, an intermediate product should be obtained. The result was a mixture of the extreme forms, with transitional shapes in every possible stage. Finally, the α-salts were found to be quite as readily attacked by nitrous acid as the β-salts. There seems, therefore, to be no positive evidence in these experiments of any essential difference.

Salts of Diamidophosphoric Acid.

Owing to the extreme solubility and absence of crystallizing power of the alkaline and earthy salts, they cannot be obtained in a form suitable for analysis. The primary salts have doubtless the general formula $PO(NH_2)_2OM$, (or possibly $P(NH)(NH_2)(OH)(OM)$; those with more base are in some cases possibly derivatives of the same acid, in others they are unquestionably diamidotrihydroxylphosphates, reacting with silver nitrate directly to form salts of this acid. They are all much more stable than the corresponding monamidophosphates.

Potassium and Sodium Salts.—By adding to 1 molecular weight

[1] This Journal **15**, 204.

free acid, 1 molecular weight potassium or sodium hydroxide, solutions are obtained, which, on evaporation in small quantities on the water-bath or *in vacuo*, leave perfectly transparent vitreous masses, readily soluble in water, but not deliquescent, insoluble in alcohol, and which are primary salts; silver nitrate precipitates from the solution the characteristic primary silver salt. With 2 molecular weights alkali, the secondary salts are formed, which have similar properties, but which give the secondary silver salt. With increasing quantities of alkali, the silver precipitate changes to yellow and finally brown, the yellow body being the tertiary salt of the pentabasic acid. As seen in the experiments on the saponification of the ether, tertiary potassium diamidotrihydroxylphosphate is converted into secondary salt by phenol, into primary salt by carbon dioxide, and into free acid by acetic acid.

Ammonium Salts.—1 molecular weight free acid is able to combine completely with 1 molecular weight ammonia; with 2 molecular weights the solution has an ammoniacal odor and gives with silver nitrate a mixture of secondary and primary silver salts.

Barium Salts.—The *primary* salt, $\left(PO\begin{matrix}(NH_2)_2\\O—\end{matrix}\right)_2Ba$, is formed by adding to the free acid the calculated amount of baryta solution, or by using an excess of the latter, and treating with carbon dioxide, or by digesting the acid with excess of barium carbonate. It is most conveniently made directly (mixed with phenol) by saponifying the ether as above described. It is extremely soluble in water, and on careful evaporation is left as a transparent vitreous mass. Alcohol precipitates it in viscous form. The solution decomposes very slowly in the cold, but quite rapidly on heating, forming a white granular precipitate; but even after boiling an hour or more, much remains undecomposed, as shown by its yielding the characteristic primary silver salt. By using 1 molecular weight acid and 1 molecular weight baryta the secondary salt is formed, which in physical properties resembles the primary salt, but which gives secondary silver salt, and is decomposed by carbon dioxide. The solutions, with excess of baryta, remain clear, and are but very slowly decomposed by boiling.

Magnesium Salts.—The free acid is not precipitated by magnesia mixture; it dissolves magnesia and decomposes the carbonate in the cold, forming primary salt. If the oxide be used, a

small quantity of secondary salt seems to form, as the solution gives, besides primary, a small amount of secondary silver diamidophosphate. A determination of the ratio in the solution gave P : Mg = 2 : 1.17, or nearly that required for $\left(PO\overset{(NH_2)_2}{O—}\right)_2Mg$. The salt resembles the barium and alkali compounds, leaving a transparent glass on evaporation, which is permanent in the air. Alcohol precipitates it as a clear liquid. On boiling, it slowly deposits a flocculent precipitate.

Other Salts.—Primary barium salt gives an abundant granular light-blue precipitate with cupric nitrate, and a white pulverulent precipitate with lead nitrate; with mercuric chloride no precipitate is formed, and with nickel and cobalt nitrates a precipitate only on long standing.

Silver Salts.

These are by far the best characterized salts observed. They have the advantages of being for the most part insoluble in water, of having sometimes characteristic crystalline form, in other cases characteristic color, of being usually free from crystal water, and of containing a univalent metal, thus giving indications as to the basicity of the acid. Some are to be referred to diamidoorthophosphoric acid, others are diamidotrihydroxylphosphates. They are all unaffected by light.

Primary Silver Diamidophosphate, $PO\overset{(NH_2)_2}{OAg}$.—This highly crystalline, very characteristic and stable salt is obtained in several ways, but most conveniently from the primary barium salt, prepared by direct saponification of the ether. To the dilute solution (which may contain a little barium dicarbonate) is added, drop by drop, the calculated quantity of silver nitrate solution, when the salt rapidly separates as a coarse white sand, which is washed, dissolved in ammonia, diluted to about one liter for each fifty grams, and precipitated by adding dilute nitric acid, drop by drop. Each drop produces a white amorphous precipitate, which at once redissolves, and presently the primary salt crystallizes out. The addition of nitric acid should be continued to neutral reaction. The yield, thus purified, is about equal to the weight of phenyl ether taken, or 85 per cent. of the theoretical. Carbon dioxide also precipitates it in apparently pure form from the ammonia solution. It loses nothing over sulphuric acid or at 100°.

	Calculated for $PO(NH_2)_2 \cdot OAg$.	Found. (1).	(2).	(3).
P	15.29	15.32	14.57	15.28
N	13.83	12.97 13.11	...	13.48, 13.44, 13.42
Ag	53.14	52.81	53.89	53.01

(1). P : N : Ag = 1 : 1.87 and 1.89 : 0.99.

(2). P : Ag = 1 : 1.06.

(1) and (2), from free acid and 1 molecular weight ammonia, (1) with calculated, (2) with large excess of silver nitrate; not recrystallized.

(3). P : N : Ag = 1 : 1.94 : 1. Prepared like (1), and recrystallized.

The analysis of this and other silver salts is best effected by dissolving in dilute nitric acid for silver and phosphorus and in hot dilute sulphuric acid for nitrogen, the solution being heated a half-hour, the silver removed by hydrochloric acid, and the filtrate distilled with alkali. *Concentrated* sulphuric acid acts violently, usually causing evolution of free nitrogen, and in some cases explosion.

Prepared as above, the salt forms a white sand, but by spontaneous decomposition of the secondary salt under water, or by dissolving either salt in ammonia and evaporating over sulphuric acid, crystals of two or three millimeters in length are obtained. The crystals are thus described by Prof. J. P. Iddings:

"The habit is sometimes short prismatic, with prism faces horizontally striated and terminated at both ends by a single, somewhat acute rhombohedron. In other cases the habit is rhombohedral, consisting of the same rhombohedron with or without small prismatic truncations of the angles. It often separates in acicular forms, which, on closer examination, are seen to consist of groups of rhombohedra united in the direction of the principal axis, and occasionally showing a tendency to form stellate and cruciform groups."

The salt is also obtained in characteristic form by dissolving any of the silver salts described below in ammonia and precipitating by nitric acid, but as the higher salts often give at first amorphous precipitates, the process has frequently to be repeated; also by digesting the free acid with silver oxide.

It is nearly insoluble in water, readily in ammonia, of which it requires exactly two molecular weights. The ammoniacal solution gives with silver nitrate a precipitate of more or less impure

secondary salt. Sulphuretted hydrogen liberates the free acid. If rapidly heated it swells up, evolves ammonia, and finally fuses to a grayish mass. If heated at 150°–160° it slowly loses weight, the loss approximating to that required by the equation

$$2PO\begin{matrix}(NH_2)_2\\OAg\end{matrix} = NH\begin{matrix}PO\begin{matrix}NH_2\\OAg\end{matrix}\\PO\begin{matrix}OAg\\NH_2\end{matrix}\end{matrix} + NH_3,$$

that is, to that required by the formation of the silver salt of *diamidopyrimidophosphoric acid.*

	Calculated Loss.		Found.
2 mols.	$-NH_3$ 4.20	After 2 hours at 150°–160°	4.65
2 mols.	$-2NH_3$ 8.40	" 6 " " "	6.11

The rapid loss of the first molecule of ammonia is accompanied by a very slow loss of the second; at 200° the rate of loss diminishes and is finally succeeded by an actual increase of weight of about 3.8 per cent., which is followed by a further loss at 230°, with fusion. Although the experiment was not carried further, observations on pyrimidophosphoric acid,[1] which will appear in a separate paper, show that its silver salt is oxidized at 200° by dry oxygen to silver pyrophosphate. The increase of weight in the above case is doubtless due to oxidation of the imido groups to free nitrogen and water, and combination with the latter to form acid silver pyrophosphate, which fuses with loss of water at 225°. The salt formed by the loss of the first molecule of ammonia will be studied further when opportunity admits, as its acid has an empirical formula identical with that of Gladstone's *pyrophosphotriamic acid*,[2] $O\begin{matrix}PO(NH_2)_2\\PO\begin{matrix}OH\\NH_2\end{matrix}\end{matrix}$, the existence of which is denied by Mente,[3] who regards Gladstone's compound as $NH\begin{matrix}PO\begin{matrix}NH_2\\NH\end{matrix}\\PO\begin{matrix}NH\\OH\end{matrix}\end{matrix}$. Both observers prepared the acid in the same manner, by acting on phosphorus oxychloride with dry ammonia, and subsequent treatment with water, and each obtained analytical data agreeing well with his own formula. If Gladstone's acid has really the formula $P_2N_2H_7O_4$, it is probably the diamide of pyrimidophosphoric acid, not the triamide of pyrophosphoric acid,

[1] This Journal **15**, 212. [2] Jour. Chem. Soc. [2] **4**, 1; [2] **6**, 68.
[3] Ann. Chem. (Liebig) **248**, 246.

and hence identical with the acid of the compound obtained by heating primary silver diamidophosphate. Experiments on phenyldichlorphosphate, above alluded to, indicate that the linkage of the two phosphorus atoms probably occurs during treatment with ammonia gas, and not by the subsequent action of water.

Primary silver diamidophosphate probably contains silver united with oxygen, this conclusion being based on the slowness with which it decomposes on heating, as distinguished from those salts known to contain silver joined to nitrogen, which deflagrate or explode, and also on the absence of color, the known nitrogen salts being colored.

A silver salt crystallizing in large colorless scales was frequently obtained by dissolving various silver diamidotrihydroxylphosphates in ammonia and precipitating by nitric acid, and also by neutralizing a solution of the free acid in caustic potash, and precipitating by silver nitrate. It forms more or less elongated plates with parallel edges and ragged ends, and quickly passes into rhombohedra of the primary salt. The exact conditions under which it forms have not yet been made out; it is perhaps the primary salt of the pentabasic acid, $P\overset{(NH_2)_2}{\underset{(OH)_2}{O}}OAg$.

Secondary Silver Diamidophosphate, or Amidophosphimate, $P(NH)\overset{NH_2}{(OAg)_2}$.—A solution containing 1 mol. wt. free acid and 1 mol. wt. barium hydroxide was poured into a solution of 2 or more mol. wts. silver nitrate, when a perfectly amorphous straw-colored precipitate was obtained. This was washed, dried on a porous plate and over sulphuric acid. It lost practically nothing at 100° and gave on analysis:

	Calculated for $PN_2H_3O_3Ag_2$.	Found.
P	10.01	9.98
Ag	69.61	71.04

or P : Ag = 1 : 2.05.

If the primary salt be dissolved in ammonia, and silver nitrate added, an amorphous precipitate is obtained, which, when an excess of ammonia has been used, is often colorless, but becomes straw-colored on washing, and frequently has this color from the first. This is doubtless the secondary salt, colorless when pure,

but usually contaminated with small quantities of the yellow salt described below. There is a strong tendency to the formation of more or less primary salt at the same time, which is easily recognized under the microscope. It has been already mentioned that diamidophosphoric acid is able to hold 1 mol. ammonia, but that with more than this the solution has an ammoniacal odor; hence it appears that the secondary salt dissociates easily. The proportion of primary and secondary silver salt formed from this solution depends on the relative amounts of acid, ammonia and silver present. Many attempts were made to prepare pure secondary salt in this way, but although some preparations seemed to be free from primary salt, the analyses were always unsatisfactory and may be omitted. One experiment only may be mentioned: 1 mol. wt. acid, 3 mol. wt. ammonia and 2 mol. wt. silver nitrate gave a curdy precipitate which was taken for secondary salt; on warming, however, it was at once converted into a crystalline powder which proved to be only primary salt:

	Calculated for $PO(NH_2)_2OAg$.	Found.
P	15.29	15.16
N	13.83	13.61
Ag	53.14	53.21

or P : N : Ag = 1 : 1.99 : 1.01.

Whenever the amount of silver was relatively increased, there was an increase in the quantity of secondary salt.

Dry secondary silver diamidophosphate, if heated, swells up, gives off ammonia and water, and leaves a residue grayish from metallic silver; it is totally devoid of explosive properties. Its solution in ammonia, if allowed to evaporate over sulphuric acid, deposits large crystals of primary salt, but no secondary salt. It shows a remarkable behavior on standing or heating under water. In the course of a few hours, dark-red specks appear in the nearly colorless amorphous mass, and in the course of a day or two the whole has become converted into a mixture of dark-red granules, and large colorless crystals of the primary salt, the change being accompanied by great diminution of bulk; the same transformation occurs in a few moments on boiling. It also occurs to a slight extent in the course of weeks or months if the salt be preserved in an imperfectly dried condition, as indicated by its acquiring a pink or reddish tint; if absolutely freed from moisture

by careful drying over sulphuric acid, it can be kept without change indefinitely.

The red substance thus formed, which is referred to hereafter as "red salt," has a color almost identical with that of silver dichromate. It is formed in several other ways, which will be described below. Although very stable, it is difficult to obtain with constant composition, and it cannot be recrystallized; hence some doubt still exists as to its nature; it is, however, certain that it contains phosphorus, nitrogen and silver in the ratio 1 : 2 : 4, and it may be provisionally regarded as tetra-silver amidophosphimate: $P(NAg)\begin{matrix}NHAg\\OAg\\OAg\end{matrix}$.

The secondary salt, in the dry state, has the formula $PN_2H_3O_2Ag_2$, which makes it a salt of diamidophosphoric acid. Its white color and the absence of explosive properties make it almost certain that the silver is wholly united with oxygen, as represented by $P(NH)\begin{matrix}NH\\(OAg)_2\end{matrix}$, *i. e.* silver *amidophosphimate.* Its mode of formation and general behavior, however, indicate rather that in the freshly precipitated, moist condition it is a true diamidotrihydroxylphosphate, $P\begin{matrix}(NH_2)_2\\(OAg)_2\\OH\end{matrix}$, which loses 1 molecule water on drying. Mixtures of free diamidophosphoric acid and alkali behave in every respect as pentabasic compounds, as will be shown below, and this salt is made from such a mixture. The strong tendency which the fresh, moist salt shows to pass into others containing more silver, is shown by the trihydroxyl compounds only; the primary salt, which is a diamidoorthophosphate, does not show it in the least.

The action of caustic potash and of ammonia on this salt will be stated below.

Action of Caustic Potash on Primary Silver Diamidophosphate. Diamidotrihydroxylphosphates.

The behavior of potassium hydroxide towards primary silver diamidophosphate leaves no doubt that diamidophosphoric acid readily forms addition-products with bases, which are salts of the diamide of pentabasic phosphoric acid. The action of alkaline carbonates, which is somewhat different, is stated in a separate

section; boiling baryta-solution acts only superficially on the silver salt. If 30-per cent. caustic potash solution be poured on the primary silver salt, a coherent white pasty mass results. It is better to add the salt in small portions to the alkali, with stirring, about 10 cc. being taken for each gram salt; as made in this way the paste is less coherent, forming small fragments. Not a trace of silver oxide is formed. On adding water cautiously, with constant *gentle* agitation, the paste swells up to transparent masses of jelly, and if about ten volumes of water have been added, this appears gradually to dissolve, and finally a solution is obtained which is as viscous as thick starch-paste or mucilage, and perfectly colorless and transparent. Portions of undissolved jelly may be brought into solution by breaking up with a rod. Further addition of water, up to a certain point, causes no visible effect further than to thin the liquid; on adding more, a yellowish tint appears, which may be destroyed by adding more potash. On diluting further, the color increases until finally a deep wine-red, transparent solution is obtained. It requires much water to bring this about, but the color is intense, one gram of silver salt giving a deep color to one liter of water.

The jelly is also obtained by adding potash solution, drop by drop, to the silver salt covered with water.

Properties of the Potash Jelly.—The clear gelatinous solution remains at first unchanged, but in the course of half an hour, or sooner, if violently shaken, it begins to grow turbid, and after several hours has deposited a voluminous snow-white mass,[1] the liquid at the same time losing its viscosity. The new body is washed with 3-per cent. potash—pure water decomposes it instantly—and is then quickly pressed out on a clay plate, transferred to another clay plate and dried *in vacuo* over sulphuric acid. Owing to the necessity of washing with potash solution, the potassium determination falls somewhat too high. Analysis shows it to be

Mono-potassium-di-silver Diamidotrihydroxylphosphate,

$P\begin{matrix}(NH_2)_2\\(OAg)_2\\OK\end{matrix} + 2H_2O$.—The substance, dried over sulphuric acid, lost nothing at 100° and gave:

[1] It is not absolutely necessary to dilute the alkaline liquid to obtain this compound; it forms directly and more rapidly, but not in as well crystallized form, in the undiluted 30-per cent. potash solution.

	Calculated for $PN_2H_4O_3KAg_2 + 2H_2O$.	Found. (1).	(2).	
P	7.72	8.23	7.72	7.59
K	9.73	...	11.68	11.69
Ag	53.68	53.57	53.39	52.84

(1). P : Ag = 1 : 1.87. Washed with 3-per cent. potash, alcohol and ether.

(2). P : K : Ag = 1 : 1.22 : 1.99. Washed with 3-per cent. potash, and dried on porous plate over sulphuric acid.

The alkaline mother-liquor, which contains no silver, on neutralizing and adding silver nitrate, gives an abundant precipitate of primary silver diamidophosphate, indicating that only a portion of the acid has gone to form the double salt. The reason for this appears from the following considerations:

The action of the potash, in forming the jelly, is doubtless simply one of addition:

$$\underset{\text{Primary Salt.}}{PO\begin{matrix}(NH_2)_2\\OAg\end{matrix}} + 2KOH = \underset{\text{Jelly.}}{P\begin{matrix}(NH_2)_2\\OAg\\(OK)_2\end{matrix}} + H_2O.$$

The double salt with two atoms silver is then formed thus:

$$2P\begin{matrix}(NH_2)_2\\OAg\\(OK)_2\end{matrix} = \underset{\text{Needles.}}{P\begin{matrix}(NH_2)_2\\(OAg)_2\\OK\end{matrix}} + P\begin{matrix}(NH_2)_2\\(OK)_2\end{matrix}.$$

The last remains in solution, and on neutralizing, gives primary potassium diamidophosphate, precipitated by silver nitrate as primary silver salt. Occasionally the scaly salt above referred to was obtained, which rapidly changed to rhombohedra of the primary salt.

The same crystalline double salt is formed by direct action of caustic potash on the secondary silver salt:

$$P(NH)\begin{matrix}NH_2\\(OAg)_2\end{matrix} + KOH = P\begin{matrix}(NH_2)_2\\(OAg)_2\\OK\end{matrix},$$

and a probably analogous sodium compound, also crystallizing in needles, is obtained from the primary salt and caustic soda; the formation of a jelly was not observed.

Mono-potassium-di-silver diamidotrihydroxylphosphate forms snow-white voluminous masses, which, under the microscope, are seen to consist of tufts of long, straight, radiating prisms. The

dried salt is usually not absolutely white. The water of crystallization is held tenaciously, and is scarcely given off below the point of decomposition. On heating, the salt decomposes rather suddenly, with a faint crackling sound, giving off much water and ammonia. It may be boiled any length of time with 30-per cent. potash, without undergoing any appreciable change except a trifling discoloration. In fact, potash of this strength converts all the other silver salts into this compound, slowly in the cold, rapidly on heating, any excess of silver above two atoms being liberated as oxide. If, however, sufficient free diamidophosphoric acid be added, the conversion is complete. Silver oxide is converted into the same salt by digesting or boiling with strong potash and diamidophosphoric acid. Even dilute potash, as 3-per cent., effects the same changes slowly *in the cold;* if, however, the liquid be boiled, the five-atom explosive silver salt is formed, which is gradually reconverted into the needles on standing in the cold. These observations explain the following: if heated in a test-tube under the mother-liquor (which usually contains about 3 per cent. potash), the needles turn yellow, then red, and then brown, at the bottom of the tube, where the heat is greatest, but on removing from the flame they instantly become white again; this chameleon effect may be repeated indefinitely. If the whole contents of the tube be allowed to become hot, the needles are wholly converted into the brown explosive salt; on cooling and allowing to stand several hours, this passes back into the colorless needles; this, too, may be repeated indefinitely.

On dissolving in ammonia and neutralizing with nitric acid, the primary salt is regenerated.

Tri-silver Diamidotrihydroxylphosphate, $P\begin{matrix}(NH_2)_2\\(OAg)_3\end{matrix} + 2H_2O$.—The above acicular double salt, if washed with cold water, becomes yellow, especially if it has been dried; if freshly prepared and still moist, it sometimes becomes yellow, but usually a yellowish-flesh color. When pure yellow, it suggests silver phosphate. This change of color is accompanied by a deep decomposition, a salt with three atoms of silver being formed, while the filtrate is found to contain potassium diamidophosphate in large quantities. The change is represented by the equation:

$$3P\begin{matrix}(NH_2)_2\\(OAg)_3\\OK\end{matrix} = 2P\begin{matrix}(NH_2)_2\\(OAg)_3\end{matrix} + P\begin{matrix}(NH_2)_2\\(OK)_3\end{matrix}.$$

The new substance is in the form of needles, which are, however, merely pseudomorphs after the potassium silver salt. Complete decomposition is difficult to effect, as no actual solution occurs; hence hot water extracts a little alkali, and the analytical results are not very close. The air-dried substance contains approximately two molecules water, which it loses but very slowly in the air, more rapidly over sulphuric acid, and at once at 100°. This and the potassium silver salt are the only amidophosphates of silver which have been found to contain crystal water.

Dried at 100° its color is orange. Three preparations, dried at this temperature, gave:

	Calculated for $P(NH_2)_2(OAg)_3$.	Found. (1).	(2).	(3).
P	7.14	7.40	7.38	7.26
Ag	74.46	74.23	73.75	74.33

$$P : Ag = \begin{cases} (1). & 1 : 2.88 \\ (2). & 1 : 2.75 \\ (3). & 1 : 2.94 \end{cases}$$

The water lost by the air-dried substance at 100°, expressed in percentage of the anhydrous substance was

	Calculated for $2H_2O$.	Found. (1).		(2).	(3).
Loss	8.28	8.09	7.69	7.60	6.71

$$P : H_2O = \begin{cases} (1). & 1 : 1.89 \text{ and } 1.79 \\ (2). & 1 : 1.77 \\ (3). & 1 : 1.59 \end{cases}$$

If free from water, as when dried at 100° or for a long time over sulphuric acid, it may be kept indefinitely without change, but if preserved after simply drying in the air, that is, with crystal water, it remains unchanged for a week or two, and then suddenly, in the course of a day or two, undergoes a change, turning red and becoming granular. It also passes gradually into a red salt when kept under water. Whether the red compound formed by this change is identical with that obtained by other methods is uncertain. It is much lighter in color, but this might be caused by admixture with a colorless substance. No free acid is formed, and microscopic examination fails to indicate the presence of primary salt. If dry, the yellow salt turns brown on heating and then suddenly deflagrates, giving off ammonia; if not anhydrous,

it turns red before deflagrating. Ammonia dissolves it with some difficulty, as is the case with the other silver diamidotrihydroxylphosphates, first turning it white; from this solution nitric acid frequently precipitates the white scaly salt, which gives rhombohedra of primary salt on boiling.

I regard this yellow salt as containing silver united with oxygen only, because of its resemblance in color to silver phosphate, assuming the color to be due to the common chromophore $=P(OAg)_3$, and because its formation would take place by a process analogous to that often occurring in the decomposition of double salts; also because it is formed by digesting the acicular mono-potassium di-silver salt with silver nitrate.

The yellowish color frequently shown by the secondary salt, and which it always takes on momentarily on heating, before passing into the red compound, is possibly to be ascribed to the formation of this body.

If boiling water be poured on the yellow salt, it is instantly transformed into a red-brown amorphous substance which, on heating a few minutes under water, changes to the red salt with 4 atoms of silver. The same change is shown by the crystalline potassium silver salt, but the product in this case is not pure, owing to the further action of the alkali. The first stage of the decomposition may be expressed by the equation:

$$4P\begin{matrix}(NH_2)_2\\(OAg)_3\end{matrix} = 3P\underset{\beta\text{-red-brown salt.}}{\begin{matrix}(NHAg)_2\\(OAg)_2\\OH\end{matrix}} + PO\begin{matrix}(NH_2)_2\\OH\end{matrix} + H_2O.$$

The β-red-brown salt then decomposes further, as described below, into red salt and water.

Decomposition of the Potash Jelly by Cold Water.

α- and β-Tetra-silver Diamidotrihydroxylphosphate, $PN_2H_3O_3Ag_4$.—The effect of diluting the potash jelly has been already described. Any lumps of jelly remaining undissolved are gradually converted into an insoluble red-brown amorphous substance. The wine-red solution is very stable, and may be kept any length of time or boiled without visible change, but is decolorized by adding a large quantity of potash. On passing carbon dioxide into the cold solution it soon becomes turbid and finally colorless, depositing a flocculent substance, which in color and general

appearance closely resembles precipitated ferric hydroxide. The action of carbon dioxide must be discontinued as soon as the precipitate has completely formed, otherwise some silver carbonate is formed. The substance is readily washed by decantation with cold water and on the filter; the washing should be thorough, as it retains a trace of alkali somewhat persistently. It is then sucked out and dried *in vacuo* over sulphuric acid, when it forms a lump with vitreous fracture, easily pulverized to a red-brown powder. It usually loses about 2 per cent. water on drying at 100°, but appears to be otherwise unchanged. The analysis of two preparations, dried at 100°, gave:

	Calculated for $PN_2H_3O_3Ag_4$.	Found. (1).	(2).
P	5.73	5.51	5.73
Ag	79.68	79.36	79.20

(1). P : Ag = 1 : 4.15.
(2). P : Ag = 1 : 3.98.

The substance dried over sulphuric acid for a few days shows some chemical difference from the freshly precipitated and still moist compound, the cause of which is not clear, but which cannot consist in a difference of empirical composition, except in as far as this may be due to loss of water. The fresh substance may be distinguished as α, the dried as β.

α-tetra-silver diamidotrihydroxylphosphate does not change by standing under cold water, but under boiling water it changes slowly, becoming more compact, and after long heating (an hour) being converted into a heavy, nearly black powder, which does not explode by friction, and which under the microscope is seen to be granular, with indications of being crystalline; no red salt is formed. A strongly alkaline solution of potassium diamidophosphate instantly converts the α-salt into needles of the potassium silver compound; potash alone, in the cold, slowly converts it into the same body, liberating silver oxide.

β-tetra-silver diamidotrihydroxylphosphate does not explode on friction; on heating it detonates rather weakly, with a reddish flash, giving a little moisture and ammonia. Dropped into strong sulphuric acid it also flashes, but gives no sound, a little metallic silver separating. When boiled with water, it changes in two or three minutes into red salt (see analysis), which contains a higher percentage of phosphorus and silver, but in the same ratio. The

β-salt is probably identical with the red-brown substance obtained by treating the tertiary silver salt with hot water, as they have the same appearance and both yield the red salt very quickly on boiling. Towards potash and other reagents it shows the same general behavior as the other salts.

For a body of the above composition but two formulas are possible:

$$\text{(a)}\quad \begin{matrix} NH_2 \\ P\,NHAg \\ (OAg)_2 \end{matrix} \qquad \text{and (b)} \qquad \begin{matrix} (NHAg)_2 \\ P(OAg)_2 \\ OH \end{matrix}.$$

A substance of formula (b) would probably lose water quite readily, giving red salt, $PNAg\begin{matrix} NHAg \\ (OAg)_2 \end{matrix}$, which is true of the β-salt. The isomeric body (a) would probably change much more slowly, and the tendency would be not to lose water but silver oxide, thereby becoming black, and this is the behavior shown by the α-salt. Such reasoning is unsatisfactory, and positive evidence of their constitution must be sought in further experiments.

The undiluted potash jelly is also decomposed by carbon dioxide, but the liquid remains colorless; there is formed a precipitate which closely resembles, and is possibly identical with the α-tetra-silver salt. By long-continued action of carbon dioxide this is finally converted into silver carbonate.

The nature of the dark-red solution there is, of course, no means of directly determining, as it contains a large excess of potash. From the solubility of the colored body we may infer that it is a potassium salt, and from its dark color that it contains silver united with nitrogen. There is no reason for supposing that it contains, like the α-precipitate, four atoms of silver, on the contrary it must contain less, as this would require at least two to be joined to oxygen, and such a body, like the white salt with two atoms of silver and one of potassium, would be insoluble.

Decomposition of the Potash Jelly by Heat.

Penta-silver Diamidotrihydroxylphosphate, $P\begin{matrix} (NHAg)_2 \\ (OAg)_3 \end{matrix}$.—If the flask containing the colorless, transparent potash jelly (diluted to a strength of about 2–3 per cent. potash) be placed in boiling water, the solution becomes red-brown, then turbid, and in a few

minutes deposits a dark-brown amorphous precipitate, which might be mistaken for silver oxide. In order to obtain it pure it is necessary to heat the liquid for about fifteen minutes at 100°, or until the precipitate appears homogeneous, otherwise it is apt to contain some of the red-brown salt and its appearance is streaky. It is then washed once or twice with boiling water, by decantation, again digested at 100° with 2–3 per cent. potash, washed with boiling water, sucked out and dried *in vacuo* over sulphuric acid. Owing to its dangerous properties when dry, it is advisable to break up the moist cake. It is not even necessary to gelatinize the primary silver salt; simple boiling with 2–3 per cent. potash suffices to effect the transformation, but it is apt to be incomplete. The substance lost nothing at 100°, and gave the following figures on analysis:

	Calculated for $PN_2H_3O_3Ag_3$.	Found. (1).	(2).	(3).
P	4.78	4.87	4.95	4.71
Ag	83.18	81.64	83.33	82.30

(1). P : Ag = 1 : 4.82. Prepared from jelly by heating only.

(2). P : Ag = 1 : 4.84. From primary salt without previously gelatinizing.

(3). P : Ag = 1 : 5.03. From jelly after *repeated* treatment with potash.

A second method consists in boiling the needles (potassium-silver salt) with dilute potash; a third in treating the tertiary silver salt in the same way; the salts with four atoms of silver undergo the same transformation. These changes may be represented as follows:

(1). $5P\begin{matrix}(NH_2)_2\\(OK)_2\\OAg\end{matrix} + 2KOH = P\begin{matrix}(NHAg)_2\\(OAg)_2\end{matrix} + 4P\begin{matrix}(NH_2)_2\\(OK)_2\end{matrix} + 2H_2O.$

(2). $5P\begin{matrix}(NH_2)_2\\OK\\(OAg)_2\end{matrix} + 4KOH = 2P\begin{matrix}(NHAg)_2\\(OAg)_2\end{matrix} + 3P\begin{matrix}(NH_2)_2\\(OK)_2\end{matrix} + 4H_2O.$

(3). $5P\begin{matrix}(NH_2)_2\\(OAg)_2\end{matrix} + 6KOH = 3P\begin{matrix}(NHAg)_2\\(OAg)_2\end{matrix} + 2P\begin{matrix}(NH_2)_2\\(OK)_2\end{matrix} + 6H_2O.$

Reaction (2) is reversible, reading from left to right when the potash is hot and dilute; on cooling, it occurs in the opposite sense, as it also does when the five-atom salt is boiled with 30-per cent. potash and diamidophosphoric acid. Reactions (1) and (3)

are not strictly reversible, but on standing in the cold, the potassium salt (3 molecules) acts on the silver salt (2 molecules), converting it in (1) wholly, in (3) partly, into the crystalline double salt, the remainder being converted by any excess of potash into the same body and silver oxide.

This salt, which appears to contain the greatest amount of silver with which diamidotrihydroxylphosphoric acid can combine, and which proves its pentabasic nature, may be safely handled or heated in moist condition, or dried at 100°; when dry it may often be rubbed quite strongly in a *smooth* agate mortar, but finally explodes unexpectedly on lightly touching, giving a reddish flash. It instantly detonates with a flash on percussion, on rubbing on a rough surface, on heating, or on dropping into strong sulphuric acid. One decigram gives a report like the discharge of a pistol, but the explosion of that amount would scarcely break a thick test-tube. Owing to the unexpectedness with which it explodes, however, it is advisable to protect the eyes when handling it, as the solid decomposition-products are thrown to a considerable distance.

The ease with which this body explodes, as compared with the other compounds, is remarkable. None of the others explode on friction, although the colored salts deflagrate or explode weakly on heating. The presence of a trace of Berthollet's compound, which, according to Raschig,[1] is silver nitride, NAg_3, is out of the question, as this is formed only in strongly ammoniacal solution, while in the present case no ammonia was present, unless it were a minute trace formed by decomposition of the diamide. More probable is the presence of a body containing the group NAg_2, which would probably be explosive, and which in small amounts would not be indicated by the analysis. It is conceivable that a small quantity of penta-silver amidophosphimate, $P(NAg)\frac{NAg_2}{(OAg)_2}$ might be formed by dehydration which would probably be explosive. The subject, which is rendered difficult by the impossibility of purifying the products, will receive further attention.

"*Red Salt*," *Tetra-silver Amidophosphimate*, $PNAg\frac{NHAg}{(OAg)_2}$? —Notwithstanding the variety of conditions under which this sub-

[1] Ann. Chem. (Liebig) **233**, 93.

stance is formed, and its great stability, none of these compounds have given greater difficulty in obtaining satisfactory analytical data. It must be remembered that with the single exception of the primary salt, none of these bodies can be recrystallized; with this exception, however, the analysis leaves no doubt as to their composition; the nature of the red salt must be inferred.

The body has been obtained in the following ways:

(1). By boiling secondary silver diamidophosphate, or by allowing it to stand forty-eight hours under its mother-liquor, or under water, whereby it is transformed into primary salt and red salt.

(2). By boiling tri-silver diamidotrihydroxylphosphate, whereby free diamidophosphoric acid and a red-brown substance, probably β-tetra-silver diamidotrihydroxylphosphate, result, the latter passing on further boiling into red salt.

(3). By boiling β-tetra-silver diamidotrihydroxylphosphate a few minutes with water.

(4). By boiling primary silver diamidophosphate with potassium or sodium carbonate; the same changes of color result as stated under (2).

(5). By boiling secondary silver salt with an amount of ammonia insufficient for complete solution; here, too, the red-brown compound is an intermediate product.

The following analyses of this salt, prepared by these methods, and dried at 100°, may be given.

By method (1):

	Found.				
	(1).	(2).	(3).	(4).	(5).
P	6.09	6.08	6.12	6.11	6.04
N	...	5.47	...	...	...
Ag	80.21	80.69	80.09	80.83	81.14

(1). P : Ag = 1 : 3.78
(2). P : N : Ag = 1 : 1.99 : 3.82
(3). P : Ag = 1 : 3.76
(4). P : Ag = 1 : 3.81
(5). P : Ag = 1 : 3.87

By method (2):

	Found.	
	(6).	(7).
P	6.05	5.98
Ag	81.06	81.34

(6). P : Ag = 1 : 3.85 (7). P : Ag = 1 : 3.82

By method (3):

	Found. (8).
P	5.84
Ag	80.71

(8). P : Ag = 1 : 3.97

In all but the last, the amount of silver is markedly below, but approximating to four atoms. In (8) the ratio is 1 : 4, and this may be regarded as the purest; it was made by boiling a sample of β-tetra-silver salt of known composition, and the figures are given for comparison. They show that the change is not a simple conversion into an isomer, but that the red salt contains more phosphorus and silver, but in the same ratio, which is only to be explained by loss of water. The same is true of all the preparations, which contain too much phosphorus and silver to be diamidotrihydroxylphosphates. The loss of water would be as represented in one of the following equations:

(a). $2P\begin{matrix}(NHAg)\\(OAg)_2\\OH\end{matrix} - H_2O = P(NAg)\begin{matrix}NHAg\\(OAg)_2\end{matrix}$

(b). $2P\begin{matrix}(NHAg)_2\\(OAg)_2\\OH\end{matrix} - H_2O = O\left(P\begin{matrix}(NHAg)_2\\(OAg)_2\end{matrix}\right)_2$

	Calculated for red-brown salt, $PN_2H_2O_2Ag_4$.	Calculated for $PN_2HO_2Ag_4$.	Calculated for $P_2N_4H_4O_5Ag_8$.
P	5.73	5.93	5.83
Ag	79.68	82.41	81.02

	Found for red-brown salt.	Found for derived red salt.
P	5.73	5.84
N	79.20	80.71
	P : N = 1 : 3.98	P : N = 1 : 3.97

If formed according to (a), it would be tetra-silver amidophosphimate; if according to (b), a derivative of pyrophosphoric acid. Although the figures agree better with the latter, the ease with which it is reconverted into primary diamidophosphate speaks in favor of (a); a pyrophosphate would probably be more stable. The nature of the compound must therefore be left undecided.

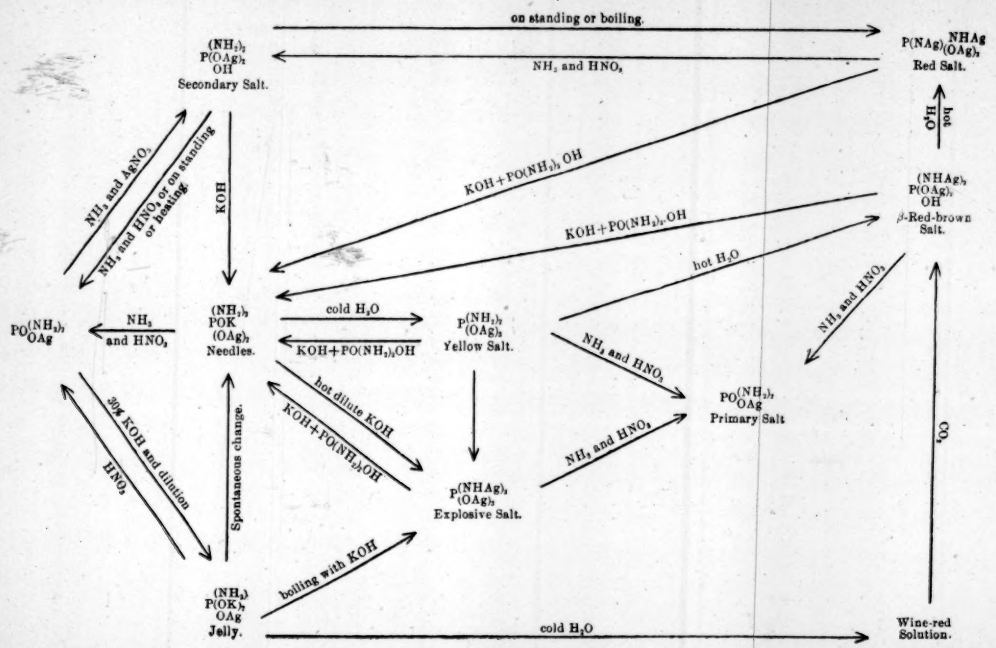
The red salt, formed from hot solution, consists of irregular granules: if formed in the cold, it forms either spherical trans-

parent grains without a sign of crystallization, or spherulites with indistinctly radial structure. It is very compact. It undergoes no change at 100°, except an occasional loss of 0.2–0.3 per cent. Heated in a test-tube it deflagrates with a red flash, but no detonation, leaving a mossy residue containing metallic silver. Dropped into concentrated sulphuric acid it flashes or becomes red-hot; at the same time there is an evolution of nitrogen and separation of metallic silver. It is difficultly soluble in ammonia, requiring a large excess and considerable time; its separation from the primary salt, when formed by method (1), is best effected by weak ammonia. The ammoniacal solution on evaporation or careful neutralization with nitric acid gives an amorphous white precipitate, probably secondary salt, which on redissolving is precipitated as primary salt, or sometimes in the form of the large scales above referred to which soon change to primary salt. Potassium diamidophosphate, in presence of potash, soon converts it into needles of the potassium-silver salt.

Action of Ammonia on Secondary Silver Amidophosphimate.—The secondary salt, if treated with an amount of ammonia insufficient for complete solution, forms a transparent pasty or slimy substance, which soon hardens to nearly transparent lumps, while the solution becomes thick, froths like soap, and gradually deposits a white substance. These transformations are doubtless due to the formation of addition-products, or double salts. On boiling, the solid is converted into an amorphous brown substance, while a similar substance separates from the solution; these change to red salt on further heating.

Action of Alkaline Carbonates on the Silver Salts.—The action of alkaline carbonates on the primary silver salt differs markedly from that of caustic alkalies, but its interpretation is similar. If the salt be covered with a strong solution of potassium or sodium carbonate, no action is apparent in the cold, except perhaps a slight discoloration. On heating, it instantly turns red-brown, and after a few minutes' boiling is completely converted into red salt, which is unchanged by prolonged boiling. No five-atom compound appears to be formed, as when caustic alkali is used.

As the primary salt is unaffected by boiling water, we must assume the formation of a silver-potassium diamidotrihydroxylphosphate and potassium dicarbonate:


on standing or boiling.
$(NH_4)_2$ $P(OAg)_2$ OH Secondary Salt.
NH_3 and HNO_3
$P(NAg)_2^{NHAg}(OAg)_2$ Red Salt.
hot H_2O
NH_3 and $AgNO_3$
NH_3 and HNO_3 or on standing or boiling
KOH
$KOH+PO(NH_2)_2OH$
$(NHAg)_2$ $P(OAg)_2$ OH β-Red-brown Salt.
$KOH+PO(NH_2)_2OH$
hot H_2O
$PO^{(NH_2)_2}_{OAg}$
NH_3 and HNO_3
$(NH_4)_2$ POK $(OAg)_2$ Needles.
cold H_2O
$KOH+PO(NH_2)_2OH$
$P^{(NH_2)_2}_{(OAg)_2}$ Yellow Salt.
NH_3 and HNO_3
NH_3 and HNO_3
$PO^{(NH_2)_2}_{OAg}$ Primary Salt
hot dilute KOH
$KOH+PO(NH_2)_2OH$
20% KOH and dilution
HNO_3
Spontaneous change.
$P^{(NHAg)_2}_{(OAg)_2}$ Explosive Salt.
NH_3 and HNO_3
CO_2
(NH_4) $P(OK)_2$ OAg Jelly.
boiling with KOH
cold H_2O
Wine-red Solution.

$$PO\begin{matrix}(NH_2)_2\\OAg\end{matrix} + K_2CO_3 + H_2O = P\begin{matrix}(NH_2)_2\\OAg\\OK\\OH\end{matrix} + KHCO_3,$$

the double salt undergoing the usual transformations into the tetra-silver salt and potassium salt, the former then losing water and forming the red body.

All the silver salts are unacted on by sodium dicarbonate in the cold, but on warming they are completely converted into sodium salt and silver carbonate.

The accompanying table shows the relations of the silver salts and their transformations.

January, 1894.

NOTE ON MONAMIDOPHOSPHORIC ACID.

By H. N. Stokes.

The researches of Gladstone[1] and of Mente[2] have shown that the action of dry ammonia on phosphorus oxychloride results mainly in the formation of complex amido- or imidophosphoric acids. Whether amides of orthophosphoric acid are formed in small amounts at the same time is left undecided by these investigators. These bodies were totally unknown at the time, and I can find nothing in their writings which would answer the question negatively.

Supplementary to a work on monamidophosphoric acid,[3] I made a few experiments in order to ascertain if this acid could be produced by the action of dry ammonia on ethyl monochlorphosphate, $PO.Cl(OC_2H_5)_2$, and if so, whether it would be a better method than that actually used.

Having satisfied myself that dry ammonia is without action on *ethyl phosphate* at 160°, and hence does not easily replace the ethoxyl group by amide, the only reactions to be expected were:

(a). $PO.Cl(OC_2H_5)_2 + 2NH_3 = PO(NH_2)(OC_2H_5)_2 + NH_4Cl.$

(b). $2PO.Cl(OC_2H_5)_2 + 3NH_3 = NH\begin{matrix}<\\\end{matrix}\begin{matrix}PO(OC_2H_5)_2\\PO(OC_2H_5)_2\end{matrix} + 2NH_4Cl.$

[1] Journ. Chem. Soc. [2] **2**, 225; **4**, 1, 290; **6**, 64, 261; **7**, 15.
[2] Ann. Chem. (Liebig) **248**, 232. [3] This Journal **15**, 198.

Analogy with the action of this reagent on phosphorus oxychloride would lead us to expect the reaction to occur only in the sense of the second equation. The theoretical increase of weight would be for (a) 19.8 per cent., for (b) 14.8 per cent.

Ethyl monochlorphosphate, which was prepared as directed by Wichelhaus,[1] was subjected to the action of dry ammonia at 0° until no further increase of weight was observed. The total increase was 17.2 per cent., or intermediate between (a) and (b). The semi-fluid mass, directly saponified with an excess of caustic soda, and acidified with acetic acid, gave an amount of primary sodium amidophosphate corresponding to about 20 per cent. of the theoretical. It seems, then, that the reaction occurs partially in the sense of equation (a), but that the yield is not so good as to make this method preferable to the other.

At 100°, the action of ammonia was totally different; instead of a gain in weight of between 14.8 and 19.8 per cent., there was a *loss* of 15.8 per cent. A combustible gas came off in streams, which, after treatment with concentrated sulphuric acid, proved to be ethyl chloride. The solid residue, which dissolved, though slowly, in water, was not further examined. The reaction

$$POCl(OC_2H_5)_2 + 2NH_3 = PO.NH_2(ONH_4)OC_2H_5 + C_2H_5Cl,$$

calls for a loss of 17.7 per cent. The cause of the evolution of ethyl chloride I am unable to explain, unless it be due to an addition of ammonia and subsequent splitting off of ethyl chloride.

January, 1894.

[1] Ann. Chem. (Liebig), Suppl. **6**, 263.

REVIEWS AND REPORTS.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. A Manual for the Examination of Soils, Fertilizers and Agricultural Products. For the use of Analysts, Teachers and Students of Agricultural Chemistry. By HARVEY W. WILEY, Chemist of the U. S. Department of Agriculture. No. 1. Easton, Pa., Chemical Publishing Co.

This notice is intended to call the attention of chemists to the work of Professor Wiley, the first number of which is now available. A review of the work is plainly out of the question at present. The publisher promises that it will appear in monthly numbers of 48 octavo pages. The following from the publisher's preface will give a clear idea in regard to its character:

"It is proposed to issue the work in two volumes. Volume I will contain a description of the origin of soils and fertilizers, and the methods of their examination. These methods embrace, first, the determinations of physical properties, *viz.* specific gravity, specific heat, heat absorption and radiation, movement of water and capillarity, flocculation and sedimentation; second, the mechanical analysis of soils, giving an account of all the methods which are practiced for separating soils into particles of uniform dimensions, with full description of apparatus employed and the manipulation required; third, an account of the official methods of chemical analysis of soils—giving especially the official methods in use by the agricultural chemists of the United States, France, Germany, Belgium and Sweden; fourth, the biological study of soils, showing the methods of detecting and isolating the micro-organisms active in the soils in influencing crop-growth, with special methods of detecting the nitrifying and denitrifying organisms; fifth, full details of the methods of examining fertilizers in use in this country and Europe.

"The first volume will be completed in about ten numbers comprising nearly five hundred pages.

"The second volume will be devoted to the best approved methods of analyzing agricultural products. The exact order of the material in the second volume has not been determined, but the main divisions will be the following: First, the determination of the carbohydrates, including starch, sugars, honeys, digestible and indigestible fiber, pentoses, etc.; second, the estimation of oils and vegetable glycerids, waxes, fats, etc.; third, the study of the several plant constituents in the form of combination in which they exist in nature; fourth, the determination of the ash of agricultural products and its composition; fifth, the general analysis of the cereals, including both grains and straw; sixth, the analysis of fruits and vegetables; seventh, the analysis of animal products,

including fresh and preserved meats, milk, butter, cheese, etc.; eighth, the examination of canned and preserved foods, with methods of detecting preservatives and adulterations therein.

"An attempt will be made to condense all the material into 24 numbers. Should, however, this be found impossible, a third volume will be issued at the same rate of subscription, *viz.* 25 cents per number.

"The estimated time for the completion of the whole work is twenty-four months. The work will be richly illustrated and will attempt to present the science of agricultural analysis in its most modern aspect. It will be issued in bound form when the final number has appeared."

INTRODUCTION À LA MÉCANIQUE CHIMIQUE. P. Duhem. Gand: AD. HOSTE. 177 pp., 1.50 francs.

The first half of this charming book is devoted to an historical account of the development of the theories of affinity and of chemical equilibrium since the time of Newton's "Optics." The process of steady growth from imperfect ideas to more correct ones, from that of affinity as gravitational cohesion to the thermodynamical theory of to-day, is most clearly and beautifully described. And the description is timely, for the contests and achievements in this work of Newton and Berthollet, Thomsen and Deville, Clausius and Horstmann, Gibbs and van't Hoff, have perhaps for us now, in the light of recent results, a still greater interest than ever before. The book is concluded by an able account of the modern thermodynamical theory of equilibrium and of the more important results which this theory has attained. The treatment is non-mathematical and is distinguished throughout by the clearness and conciseness which characterize the thinking and writing of this brilliant mathematical physicist.

J. E. T.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. Leipzig: Engelmann (1889–93).

This set of classical papers, edited by Ostwald, is a series of neatly bound and inexpensive little books, certain to be of great service to students of the physical sciences. Although the present splendid development of exact science is doubtless largely due to improved methods of instruction, yet these methods still seem to be lacking in an important particular, the cultivation of the historical sense. This requires a knowledge of the important original papers upon which the sciences are based, and these sources are often diffi-

cultly accessible. To make them more readily so is the object of the present handy collection. Papers not originally appearing in German have been carefully translated into that language, and to all there have been appended most interesting and valuable annotations. The average price of the volumes is about mark 1.40, or 35 cents. Additional numbers appear from time to time. Of about forty now issued the following have especial interest for the student of chemistry:

Helmholtz: Erhaltung der Kraft, (1847).
Dalton and Wollaston: Grundlagen der Atomtheorie, (1803–1808).
Gay-Lussac: Untersuchungen über das Jod, (1814).
Avogadro and Ampère: Grundlagen der Molekulartheorie, (1811–14).
Hess: Thermochemische Untersuchungen, (1839–42).
Kant: Theorie des Himmels, (1755).
Saussure: Untersuchungen über Vegetation, (1804).
Hittorf: Wanderungen der Ionen, (1853–59).
Woehler and Liebig: Das Radikal der Benzoesäure, (1832).
Liebig: Die Constitution der organischen Säuren.
Bunsen: Die Kakodylreihe, (1837–43).
Pasteur: Die Asymmetrie, (1860).
Wilhelmy: Einwirkung der Säuren auf den Rohrzucker, (1850).
Cannizzaro: Theoretische Chemie, (1858).
Bunsen and Roscoe: Photochemische Untersuchungen, (1855–1859).
Berzelius: Die Verbindungsgewichte, (1811–12).
Carnot: Die bewegende Kraft des Feuers, (1824).
Pasteur: Prüfung der Lehre von der Urerzeugung, (1862).

J. E. T.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. Beckurts, R. Benedikt, C. A. Bischoff, E. F. Dürre, J. M. Eder, C. Häussermann, G. Krüss, M. Märcker, W. Nernst, F. Röhmann, herausgegeben von RICHARD MEYER, Braunschweig. II Jahrgang, 1893. Braunschweig, Viewig. xii + 583 pp. 8vo.

The second annual volume of this excellent work, which was published about the middle of 1893, contains most valuable reports on the work done in the field of chemistry during 1892. The editor is thus keeping his promise of prompt publication. The book is one that is essential to every working chemist, no matter how carefully he may read other journals as they appear. Even the most conscientious may miss something of interest, notwithstanding the "Referate" of the "Berichte," and the "Abstracts" of the "Journal of the Chemical Society." A careful examination

of the "Jahrbuch" will help us to keep informed in regard to work in fields other than those in which we may be most directly interested. We ask for no better guide to the work in physical chemistry than Professor Nernst; and so too we may regard ourselves as fortunate in having Professor Krüss to point out to us the important things in inorganic chemisty; Professors Eder and E. Valenta to tell us about progress in photography; and Professor Richard Meyer, the editor, to arrange systematically the results achieved in the field of chemistry of tar and dyes. Others will turn first to the chapters on pharmaceutical chemistry and the chemistry of foods; on the technology of fats; on metallurgy; on fuel, water, technical inorganic chemistry and explosives; on agricultural chemistry and the technology of carbohydrates and fermentation; or on physiological chemistry.

I. R.

A GUIDE TO STEREOCHEMISTRY. By ARNOLD EILOART, Ph. D., B. Sc. New York: Wilson. 102 pp. 8vo.

The author has published in book form the reviews of stereochemistry which have appeared in this Journal, adding to them a comprehensive index of the subject, and a description of his models for use in teaching organic chemistry (this Journal **13**, 559). The book is to be recommended as a concise statement of the various stereochemical hypotheses, and for its full references to the original articles.

ADDRESS OF EMIL FISCHER BEFORE THE BERLINER AKADEMIE DER WISSENSCHAFTEN.

On the occasion of his installation as a member of the Berlin Academy of Sciences, Professor Emil Fischer, the successor of Professor A. W. von Hofmann, delivered an address which must be of interest to all chemists on account of its thoughtful and suggestive character. A translation[1] is here given.

In being chosen thus early in life as a member of your Academy, I am aware that I must see more of a recognition of the general branch of study I represent than of my own endeavors. To point out clearly the branch of study in which I am engaged, a hasty review of the progress of chemistry within the last quarter of a century seems to be called for.

When the distinguished scholar and investigator whom I am to succeed represented the state of his science to you twenty-eight

[1] Prepared by G. F. Weida.

years ago, it had just come to a period of quiet development after a stormy period of confusion, including the fall of dualism and the struggle between the radical and type theories. The conceptions of atom and molecule had become clear; equivalency had been extended to include valency, and in the ideas of structure the germs of good in the older theories had found a good soil for development.

Since then chemistry has been busying itself in confirming the ideas then advanced, in extending them, and in applying them to various practical problems.

As an immediate consequence of the knowledge of the true atomic weights, we have the periodic system of the elements, which has given rise to a great deal of experimental work. The conclusions drawn from it have been verified by the discovery of three new elements previously predicted by its aid, by many new investigations on atomic weights, and by many analogies (that had before been overlooked) between the elements. More than ever one may hope that this system will succeed in showing the relations between the elementary substances.

Under the influence of our views of "structure," all the branches of physical chemistry—treating of the dependence of properties of substances on their chemical composition—have flourished; and more and more the physical constants of bodies are regarded, not as accidental properties, but as valuable adjuncts in the determination of chemical constitution.

The increasing need of methods for the determination of atomic weights has brought forth our improved pyro-chemical and cryoscopic methods, in regard to which one may well doubt which is the more to be admired, their simplicity of construction or their general applicability. Cryoscopic methods, further, have opened a new bridge between chemistry and molecular physics, which has made it possible to extend the laws of gases to solutions, and to develop a simple theory of solution.

The results of work with the calorimetric bomb have, meanwhile, reached wonderful accuracy; and thermo-chemistry has amassed a large number of facts which may serve as valuable foundations for future dynamical consideration of chemical reactions.

But all these acquirements are surpassed, if not in value, at least in amount, by the progress of organic chemistry. As the ideas of structure originated in organic chemistry, so, too, in that field they have had their greatest triumphs. The carbon compounds apparently infinite in number—which in variety of composition and properties far exceed the number of forms of organized life—are by means of this theory arranged in such a system as even a morphologist might envy us. From the fundamental conception that the single atoms of the molecule are joined together in a definite order, experimental investigation gathers

courage to determine the structure of even the most complicated compounds by successive decompositions.

If in these attempts the chemist resembles the anatomist, he does on the other hand not shrink from the difficult task of being the architect who is again to bring forth the original structure from these shattered decomposition-products. Supplied with an abundance of beautiful methods, synthesis has become the characteristic of organic chemistry. The compounds that are prepared every year, filling up gaps in the system, are thousands in number. The most complicated substances of the animal and the vegetable bodies, such as coloring matters, alkaloids, carbohydrates and terpenes, have become subject to synthesis; and supported by an especially vigorous industrial development, it pushes forward impetuously into fields which are really the exclusive chemical domain of the living organism.

Hand-in-hand with the improvement in the experimental methods has gone the extension and deepening of theoretical conceptions. As evidence of this, we may refer to the latest hopeful child of speculation—stereo-chemistry.

Beginning with observations on the optical rotatory power of many organic substances, it has within the last ten years secured a firm foothold in our science, especially through the study of unsaturated compounds and of the sugars. Already successful attempts have been made to introduce nitrogen into stereo-chemical speculations, and preliminary attempts to extend similar ideas to the metals are not wanting.

We confidently expect to obtain from the further development of stereo-chemical considerations what was in vain expected of isomorphism by our predecessors, *viz.* information in regard to the space relations of the molecule, and perhaps of the individual atom. With that, the morphological part of chemistry would essentially be completed, and even to-day the difference between the ideas of constitution (extended by stereo-chemical conceptions) and the original atomic conceptions of Dalton is scarcely less than the difference between the anatomy of Vesal and the modern study of tissues.

It is not astonishing that the soil on which such fruits ripen invites workers, and we need therefore not be astonished that for the last two generations organic chemistry has received principal attention.

I too belong to this majority. Although originally feeling more inclined toward physical studies, I was led into organic chemistry through the influence of my teacher, A. von Baeyer, and since I have entered it I could not again free myself from its magic charm.

I am still of the opinion that organic chemistry, notwithstanding the immense increase of interest in the direction of physical chemistry, will (at least for some time) retain its prestige, and that the complaint that for its sake the other branches of our science are neglected is without justification.

To be sure, not all the problems of chemistry can be solved by a study of carbon compounds alone; but it is quite as certain that in the near future the most points of value in the development of theories will come from the material furnished in this field.

Therefore I would compare our science in its present condition of development to a country where a narrow, highly cultivated coast district is bordered or limited by uninhabited mountains. But up to the mountains extends the slowly sloping fruitful valley of organic chemistry. The majority of the colonists settle here, and some ambitious ones seek to find at once the path to the mountains. The hope of reaching from this valley the pass visible in the distance which will open up a new vast expanse of territory is more tempting to some, among whom I would class myself.

Since the fundamental work of Lavoisier, chemists have sought by the study of organic compounds to ally themselves to the biological sciences. In view of the magnificent discoveries of Liebig, Pasteur and others we cannot complain that the work was wanting in results. But as long as we know little more than the percentage composition of the most essential of the life products, the albuminoids; as long as we cannot explain the simplest processes that are effected by organized life, such as the assimilation of carbon dioxide by green plants and its conversion into sugar; so long we must admit that physiological chemistry is still in its infancy.

Will it ever be in a position to follow the complicated changes of the plant and animal organism and to fix their influence on morphology? Will it be possible to regulate the economy of our body when disturbed by disease according to strictly chemical principles, and thus realize the dreams of the alchemists in regard to the elixir of life? I do not doubt it. But the help for the accomplishment of this progress must be furnished to physiology by organic chemistry, and this appears to me to be such an important problem that, according to my ability, I shall take part in it. But we must not forget that this end can be reached only by the complete analysis and synthesis of the albumens, and that this alone, notwithstanding the advantages of our times, may demand the work of several generations.

Each individual worker must therefore content himself for the present to carry up the stones for the future edifice, but even in this modest way I hope to be able to show appreciation of my election by this Academy which extends its hand to the most widely differing sciences for common work.